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THE AFFINITY-CONSTANTS OF WEAK ACIDS AND THE HYDROLYSIS OF SALTS.

BY R. W. WOOD.

In a preliminary paper published in this Journal,[1] a method was described for determining the apparent action of salts on the affinity-constants of weak acids. The method was for the qualitative recognition of ionic hydrogen or hydroxyl in aqueous solutions, by measuring its retarding action on diastatic fermentation. The method is essentially as follows: A weighed amount of diastase is allowed to act for a given length of time, at a given temperature, upon a weighed amount of starch, in the presence of known amounts of acids or salts. The action of the diastase is inhibited by acids and alkalies, and by determining the amount of sugar formed in each case the retarding power is measured. The numerical results published in the first paper are of qualitative value only, for it has since been found that slight variations in temperature, not sufficiently guarded against in the earlier work, had a far greater influence than was supposed.

It was shown in the earlier paper that very small quantities of alkalies could be detected, a $\frac{N}{40000}$-solution of sodic hydrate producing a measurable retardation. Very small amounts of acids can be detected also, and the retarding power seemed to be proportional to the quantity of the acid and its affinity. In the pres-

[1] 15, 663.

ence of the neutral sodium salt of a weak acid, a much larger amount of the acid is required to produce the same effect. This is probably due to two factors: one, the partial prevention of the dissociation of the acid by the presence of its salt; the other more complex: part of the salt dissociates hydrolytically, takes up water, forming free acid and base (the former is but little dissociated, the latter practically completely); the free hydroxyl ions neutralize an equal number of the hydrogen ions coming from the large excess of acid.

In acid solutions it was found that, although 55° is the most favorable temperature for diastatic action, a much larger yield of sugar is obtained at a somewhat lower degree, showing that the inhibitory effect varies with the temperature, changes of which affect the acid more than the diastase. For accurate work the temperature should not vary a quarter of a degree. Even with the apparatus described in this paper, slight variations occur, though in the main the results are reliable.

In the earlier work the diastase, mixed with a little water, was put into an air-bath heated by boiling acetone; the starch paste containing the acid or alkali and heated to the proper temperature, was then poured upon the diastase and the cover put on. To stir the contents it was necessary to remove the cover occasionally, thereby lowering the temperature considerably. In addition to this the starch, being more or less viscous, could not well be brought to a uniform temperature owing to the absence of convection currents, and in pouring, it suffered a lowering of temperature.

By means of specially constructed apparatus, all, or nearly all, of these difficulties were overcome, and as it seems probable that the device may be useful in other lines of work, I shall describe it briefly.

A large rectangular tank (*A*) of galvanized iron, having a capacity of forty gallons, was made, within which was fastened, by means of lateral braces, a smaller tank or box (*B*), with only a narrow rim projecting above *A*. The metal cover of this inner chamber was lined with asbestos board, and covered on the outside with a thick layer of steam-pipe felting. Through this box, side by side and close together, passed two brass rods *C* and *D*, which projected into the pocket *E* through two holes in the end of the chamber. This pocket prevented the water, with which the

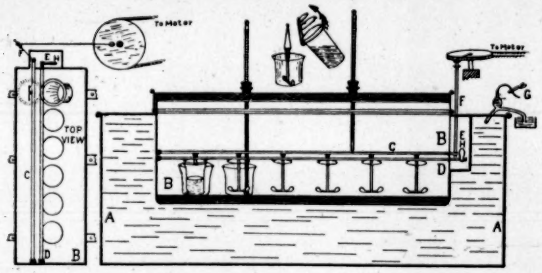


FIG. 1.

outer bath was filled, from entering the holes, and did away with the necessity of making water-tight stuffing boxes. In the diagram the rods are shown one above the other; in reality they were on a level and close together, as shown in the "top view." From the rod *C* hung six glass pendulums, which were inserted into short bits of rubber tubing fastened to the rod; they could thus be easily removed and replaced by bending the tubes a little. The end of the rod *C* was fastened to an upright pin *F*, which was geared by a simple crank to a horizontal wheel, turned by a small water-motor, which gave the six pendulums a rapid swinging motion. To the other rod were fastened six brass rings in a horizontal position (best seen in the "top view,") and the end of this rod which projected into the pocket was provided with a handle *H*. The outer bath was filled with water, which was kept at a constant level within a quarter of an inch of the edge, by the device shown at *G*, consisting of a siphon, with a bulb blown on to the bend to collect the air dissolved in the water and liberated by the warmth. This would otherwise fill the tube and stop the action. This siphon dipped into a vessel that was kept full of water by a small stream which flowed constantly.

It was necessary to suck the air out of the bulb every few days by means of a short bit of rubber tube, kept closed by a pinch-cock. This device worked perfectly, while the Mariotte bottle and a number of other schemes failed to give satisfaction. The outer bath was covered with felt and heated by two small burners regulated by a thermostat.

The apparatus is used as follows: Six beakers each containing 0.01 gram of diastase and 5 cc. of water were arranged along the side of the air chamber resting on felt, with the pendulum stirrers hanging in them. Six other beakers containing 75 cc. of starch paste at 60° C., together with varying amounts of the salt or acid to be investigated, are suspended in the brass rings. The arrangement is best seen between the thermometers in the small sketch. The cover of the air-bath is then put on, and while its temperature is rising to 53° the paste cools down from 60° to about the same degree. At the end of half an hour the air-bath, paste and diastase will have come to the same temperature, and equilibrium is established. The motor is then started which sets the pendulums swinging, and exactly at the commencement of a minute the handle *H* is turned through an arc of 90°, which empties all six beakers of starch simultaneously into the beakers of diastase. Six determinations can thus be made at once, under exactly the same conditions: there is no loss of heat by pouring; the temperature is constant throughout the experiment, and the action of the diastase can be stopped at the end of a definite time by simultaneously emptying into the beakers six small glass tubes, fastened on a frame, and containing a strong solution of sodic hydrate. The glass pendulums can be removed from the air-bath with the beakers, by slipping them out of the rubber tubes, and the solution adhering to them washed into the glasses. The contents are then made up to 100 cc. and the sugar in each determined volumetrically as before by Fehling's solution.

The diastase was prepared from barley malt as described in the preliminary paper, except that the filtering of the aqueous solution was much more rapid, and the diastase, precipitated by alcohol, was more energetic in its action than that used in the previous work, converting about 80 times its weight of starch into maltose in twenty minutes at 55° C. Bermuda arrowroot was used as before for the preparation of the starch paste.

If comparable results are to be obtained in work of this kind it is absolutely necessary that the starch shall be present in sufficient quantity to insure the yield of sugar being proportional to the time, and the amount of diastase present. In the previous work 0.01 gram of diastase was allowed to act for thirty minutes upon 2 grams of starch. Careful experiments were made with these amounts for various lengths of time, and it was found that taking the time in minutes as ordinates and the amounts of maltose formed

as abscissæ, the yield up to 25 minutes was represented by a straight line; the curvature of the line beyond this point showed that the yield was no longer proportional to the time, owing to the decrease in the quantity of starch. In order to be absolutely sure, 20 minutes was taken as the proper time for each experiment.

Effects of Changes of Temperature.

55° C. has been shown to be the most favorable temperature for diastatic action; above or below this point there is a falling-off in the yield of sugar. In the case of acid solutions, however, it was found that the maximum yield was produced at a lower temperature, indicating that the inhibitory action of the acid increased with the temperature more rapidly than the activity of the diastase. A number of experiments were made to determine the exact effects of variations in temperature in the presence of both acids and alkalies. Sodic hydrate and acetic acid may be taken as examples. The sodic-hydrate solution contained 0.0008 gram to the cc. 0.1 cc. of this solution in 80 cc. of starch—corresponding to a $\frac{N}{40000}$-solution—gave a perceptible retardation. Determinations were made with varying amounts of the alkali at temperatures of 45°, 49°, 51°, 55° and 57°. When no alkali was present the maximum yield was obtained at 55°. The results were plotted on coordinate paper, the yields of maltose being taken as abscissæ, and the amounts of alkali as ordinates. Curves were drawn for each of the above-mentioned temperatures, and although each curve started from a different point on the axis of abscissæ, owing to the effect of temperature on the diastase in neutral solution, it was found that the curves invariably flattened or approached the axis of abscissæ with an increase of temperature, showing that the inhibitory action of the alkali increased with the temperature.

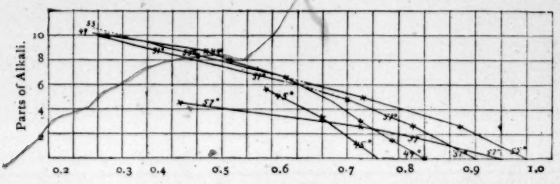


FIG. 2.—Effect of Change of Temperature on Sodic Hydrate.

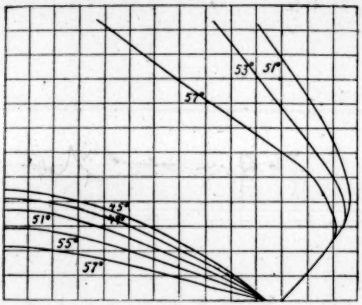


FIG. 3.—Effect of Change of Temperature on Acetic Acid (above) and Sodic Hydrate (below). Curves started from same point.

To eliminate the effects of the temperature on the diastase, and to represent graphically the effects of the temperature on the alkali, the curves were started from the same point. The regular approach of the curves to the axis of abscissæ was thus rendered more apparent, crossing of the lines being obviated. Acetic acid acted in general in the same way, but the effects of changes in the temperature appeared to be much greater than in the case of the alkali, as will be seen in the diagram. These results show the necessity of working under exactly the same conditions, for a change of 0.5° in the temperature may be equivalent to a change of ten per cent. or more in the amount of the acid.

Affinity-Constants of Acids.

The action of the fatty acids on diastase was tried, with a view of determining the affinity-constants, and comparing them with the figures obtained by other methods. Hydrochloric acid was first tried, to obtain a standard for comparison. The solution was made equivalent to the sodic hydrate (0.0008 gram to the litre) by titration with phenolphthalein. For convenience I shall call 0.1 cc. of this solution one part. Quantities up to 0.6 cc., or 6 parts, were found to produce an increased yield of sugar. This effect has been noticed by Duggan[1] and others, and is probably due to a slight alkalinity of the starch. Above this point the acid

[1] "On the Determination of Absolute Neutrality": This Journal **8**, 211.

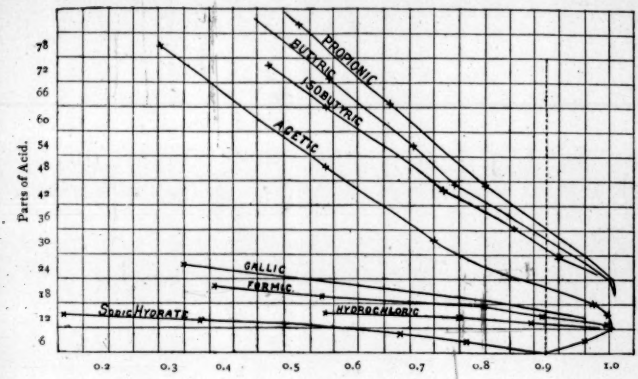


FIG. 4.—Action of Acids.

retarded the action of the diastase very much more than an equivalent amount of alkali, 10 parts reducing the yield of sugar almost to zero. This seems to show that the hydrogen ions have a much greater effect on diastase than the hydroxyl. Experiments on saponification show the hydroxyl to be more active than the hydrogen. On referring to the curves illustrating the action of acids, it will be seen that the same retardation is produced by ten parts of hydrochloric acid as by six parts of sodic hydrate. From the 10 parts we must subtract 6, that amount being used in neutralizing the starch, and we find that 6 parts of sodic hydrate are equal to 4 parts of hydrochloric acid. The actions of formic, acetic, butyric, isobutyric, propionic and gallic acids were carefully investigated and the results plotted on coordinate paper. The curve for acetic acid may be taken as typical of the others, and was investigated more carefully than the others in the vicinity of the point of maximum yield. Starting with a yield of 0.9 gram of sugar in the presence of no acid, the addition of three parts of acid gives a yield of 0.96 gram; six parts, 1.1 gram; nine parts, 0.99 gram; twelve parts, 0.97 gram; twenty-seven parts, 0.72 gram, etc.

The maximum yield of sugar is obtained when six parts of acid are present, as was the case with hydrochloric acid, consequently

six parts must in every case be subtracted from the total amount to allow for the alkalinity of the starch.

Starting with the assumption that in the case of hydrochloric acid all the molecules are dissociated, and that the retardation is due to the hydrogen ions, it is reasonable to suppose that a solution of a weak acid which exerts the same retarding power as a certain solution of hydrochloric acid contains as many dissociated molecules as there are molecules of the strong acid, from which we can determine the percentage of the acid which has suffered dissociation, and from this may be calculated, with the aid of the formula $\frac{m^2}{(1-m)V} = K$, the affinity-constant of the acid. This constant was determined for the five fatty acids investigated, and considering the wide range of experimental error involved in the investigation of so strong an acid as hydrochloric, the results agree very well with those obtained by other methods. K was calculated for acetic acid at three different dilutions, with results as follows: 10.5 parts of hydrochloric acid produced the same retardation as 45 parts of acetic; subtracting 6 from each, we have $4.5HCl = 39C_2H_4O_2$. This amount of acetic acid in 80 cc. of paste represents a $\frac{N}{1020}$-solution. On the assumptions just made, the percentage of acetic acid dissociated will be represented by $\frac{4.5}{39}$, or 0.115, from which by calculation we find $K = 0.0000146$. Alongside the results obtained by this method I shall set down the results obtained by Ostwald by the measurement of electrical conductivity:

Action on Diastase.			Electrical Conductivity.		
V.	*m.*	*K.*	*V.*	*m.*	*K.*
579	0.087	0.0000143	512	0.0914	0.0000180
1020	0.115	0.0000146	1024	0.126	0.0000177
2100	0.158	0.0000141	...	...	...

The results obtained give for K a lower value than has been assigned by other observers, but the fact that it is a nearly constant quantity seems to indicate that the principle involved in the method is correct, though owing to the difficulty of getting reliable figures with hydrochloric acid as a standard for comparison it is far less suitable for the determination of affinity-constants than other methods. The values of K for the other acids were found to be as follows:

Formic	0.025
Isobutyric	0.0008
Butyric	0.00071
Propionic	0.0006

the values being in the same order as those obtained by Ostwald with the exception of the two butyric acids, which he found to have nearly the same value. These results are certainly interesting as confirming previous work and theories, and also showing the degree of accuracy that can be obtained by this method under proper conditions.

Hydrolysis of Salts.

The neutral sodium salts of the weak acids have a strong inhibitory action on diastase, while the salts of strong acids have little or no effect. This is probably due to hydrolytic dissociation of the salt, a small portion of which takes up water, forming free acid and free base, which exist together in the solution; the former is but little dissociated, while the latter completely breaks up into Na and OH ions. By comparing the action of these salts with sodic hydrate, in the same manner as we compared the weak acids with hydrochloric, we can determine the amount of free hydroxyl, and therefore the percentage of the salt that has suffered hydrolysis. A solution of sodium acetate was made of such a strength that 1.2 cc. contained 0.082 gram of the salt. This amount in 80 cc. of starch gives a $\frac{N}{80}$-solution and inhibits the diastase to a degree corresponding to 0.000536 gram of sodic hydrate, which is the equivalent of 0.0011 gram of sodium acetate, or 1.34 per cent. of the whole amount. With double the amount of the salt, or a $\frac{N}{40}$-solution, we get a retardation corresponding to 0.00056 gram of sodic hydrate, which shows that 0.72 per cent. of the salt has suffered hydrolysis, while in a $\frac{N}{10}$-solution the percentage is reduced to 0.16. These results show that increasing the amount of the salt beyond a certain point does not increase the amount of the hydrolyzed portion to any great extent. Shields[1] made a number of determinations of hydrolysis by observing the speed at which ethyl acetate was saponified by the salt solution. Most of his work, however, was done with salts of exceedingly weak acids, which cannot be investigated to advantage by means of diastase, for in the weak solutions which must neces-

[1] Ztschr. phys. Chem. **12**, 167.

sarily be used, practically all of the salt is hydrolyzed, and we find the action the same as that of a base. In other words, when the solution is made of sufficient strength to insure that only a portion of the salt suffers hydrolysis, the action of the diastase is entirely prevented. Shields made one determination, however, with sodium acetate in a $\frac{N}{10}$-solution, and found the percentage hydrolyzed to be 0.008, a much smaller amount than is indicated by the action of the salt on diastase. He also made a determination with borax, working with a $\frac{N}{32}$-solution. A solution of this strength is unsuitable for work with diastase, but determinations were made with much more dilute solutions. A $\frac{N}{1200}$-solution acted like an equivalent amount of sodic hydrate, as did also an $\frac{N}{8040}$-solution, showing that at these two dilutions practically all of the salt was hydrolyzed. In a $\frac{N}{800}$-solution 12.4 per cent. was found to be hydrolyzed, and from this determination was calculated the dissociation for a $\frac{N}{32}$-solution, which was found to be about 0.5 per cent., agreeing fairly well with 0.9 as determined by Shields by a totally different method. The hydrolysis of salts of the other fatty acids was determined approximately, and it was found that the percentage hydrolyzed was proportional to the affinity of the acid, being greater in the case of weak acids than of stronger. No very careful or extended tables were prepared. The sodium acetate was prepared by neutralizing a sodium-hydrate solution of known strength with acetic acid, using phenolphthaleïn as an indicator. Care was taken to get the salt a trifle acid rather than alkaline, since the effect of a mere trace of acid in the presence of so large a quantity of salt would be very slight, the salt preventing dissociation of the acid. The sodium salts of the other fatty acids were made in the same way, solutions neutral to phenolphthaleïn being considered neutral. This of course was a purely arbitrary standard, for all the solutions contained ionic hydroxyl as a product of hydrolysis, and were consequently alkaline in one sense of the word.

Action of Salts upon the Corresponding Acids.

In the preliminary paper brief mention was made of the action of salts on the corresponding acids. It was shown that, in the presence of a salt of a weak acid, very large quantities of acid could be added without affecting the diastase except to a very limited degree. Owing to the uncertainty that was felt regarding the exactness of the numerical results obtained, and the absence of concordance in

many cases, no discussion was made of their theoretical bearing. Recent and more exact results show perfect agreement with theory and corroborate the views held by Arrhenius and Ostwald. In the earlier work it appeared that in the presence of 0.082 gram of sodium acetate, which alone produced a considerable retardation, the maximum yield was obtained when $\frac{1}{6}$ of an equivalent of acid, or 0.01 gram, was present, whereas this amount of acid alone would prevent diastatic action altogether. Above this point acid could be added to the amount of 1.5 equivalents, without producing any apparent action on the diastase, then it began to retard, but not nearly in the degree that it would if no salt were present. In the earlier paper the opinion was expressed that possibly as soon as sufficient acid was present to give the maximum yield, *viz*: $\frac{1}{6}$ equivalent, a further addition would cause instant retardation, but the retardation was too slight to be detected. A repetition of the work under more favorable conditions shows this surmise to be correct. The results obtained with acids in the presence of their neutral sodium salts were plotted on coordinate paper; the yields in maltose being taken as abscissæ, and the equivalents of acid in excess of the salt as ordinates. An inspection of these curves shows at first glance that the strong

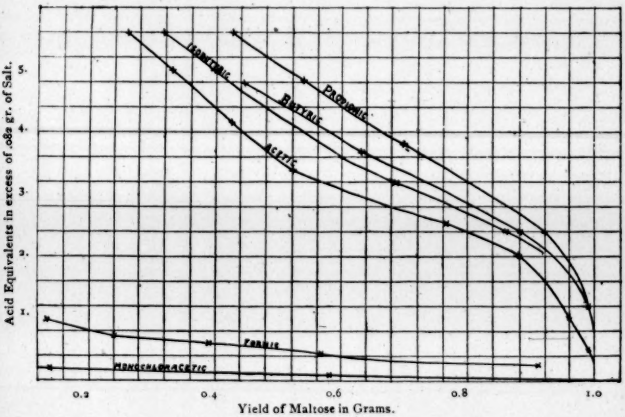


FIG. 5.—Action of Salts on the Corresponding Acids.

solutions of the acids, in the presence of their salts, act on diastase in almost exactly the same way as would a solution of the acid alone of about $\frac{1}{40}$ of the concentration, and it was found that by doubling the amount of the salt, twice the amount of acid could be used. The work of Arrhenius[1] indicates that the presence of a salt in a solution of its acid prevents the dissociation of the latter to a degree depending on the amount of salt present. In a solution of given strength, the ratio of the non-dissociated portion to the product of the ions is a constant. In an acid HA of concentration X, the formula becomes $\frac{\overset{+}{H} \times \overset{-}{A}}{X - \overset{-}{H}} = K$, or, $\overset{+}{H}$ and $\overset{-}{A}$ being equal, $\frac{H^2}{X - H} = K$. When a salt is added it is immediately dissociated, thereby adding to the number of negative ions. H is no longer equal to A and we must use the first equation or, if $X = 1$, $\frac{\overset{+}{H} \times \overset{-}{A}}{1 - H} = K$. This shows that the percentage of acid dissociated is lowered. Taking acetic acid as an example, we have $\frac{\text{Hydrogen} \times \text{Acetyl}}{\text{Undis. acid}} = K$. Sodium acetate breaks up almost completely into sodium and acetyl, thereby increasing the acetyl factor in the equation. The hydrogen factor must diminish in proportion—in other words, the percentage of acid dissociated must become smaller. Arrhenius, by noticing the rate at which saponification was produced by an acid in the presence of its salt, measured the diminution in the dissociation of the acid and found that it agreed perfectly with the diminution calculated from the above formula. If with a given amount of salt and varying amounts of acid we calculate the percentage of acid dissociated, we find that, within certain limits at least, it is a constant—in other words, if we double the amount of the acid we double the number of free hydrogen ions, and would expect the action on the diastase to be increased proportionately. This is exactly what we find to be the case as will be seen by the curves, for those representing the action of large amounts of acids in the presence of salts resemble closely those produced by small amounts of acids by themselves. Using the tables published by Ostwald, showing the percentage of dissociation of acetic acid at

[1] Ztschr. phys. Chem. 5, 1.

various dilutions, I have calculated the percentage that would be dissociated when 0.5, 1, 2, and 5 equivalents of acid were present in the excess of 0.082 gram of salt, the solutions being $\frac{N}{160}$, $\frac{N}{80}$, $\frac{N}{40}$ and $\frac{N}{16}$ respectively, and found 0.00142 to represent the fraction of the acid dissociated in each case. By multiplying this fraction by the amounts of acid present we determine the actual amount dissociated in each case, and find these amounts to be 0.0000426, 0.0000852, 0.000166 and 0.00042 gram respectively. Referring to the curves for acetic acid alone, and calculating from Ostwald's table the amounts dissociated of quantities producing the same retardation as the 1, 2, and 5 equivalents in excess of the salt, we find them to be 0.000016, 0.0002 and 0.00068—results somewhat higher than the calculated ones, but close enough to show that the theory is correct and to furnish interesting corroboration of the results obtained by Arrhenius.

The curves showing the action of salts on acids indicate fairly well the relative affinity of the acids, better, I think, than the curves for acids alone, for we are dealing with larger quantities and there is less chance of experimental error. It seems probable that diastase may be useful for determining the affinities of such substances as cannot well be determined by other methods, the organic bases for example, about which much doubt exists. It is not very suitable for measuring the constants of acids, particularly those stronger than formic, but these have practically been settled by Ostwald. I think that for accurate work there should be six thermometers dipping into the beakers in which the reactions take place, so that the temperatures of each can be read throughout the experiment. In the experiments described two thermometers were used, one dipping in a breaker, the other exposed to the air of the inner chamber, but even under the favorable conditions for uniformity it was impossible to be sure that there was not a small difference in temperature, perhaps 0.2°C.

In conclusion I wish again to express my thanks to Dr. Felix Lengfeld for his kind assistance in advising me throughout the progress of the work.

THE COLOR OF SALTS IN SOLUTION.

By J. H. Kastle.

The color of salts in solution has formed the subject of several interesting investigations, and especially in the light of recent developments in chemical theory has been the source of a good deal of speculation. Concerning this subject we find several suggestive paragraphs in Ostwald's Treatise on Solutions, an admirable translation of which has been placed in the hands of English-speaking peoples by M. M. Pattison Muir. About the time that this translation made its appearance I was engaged upon the colorimetric study of a solution of iron nitrate, with the view to determining, if possible, the extent of the decomposition of this salt in aqueous solutions by color-measurements alone.

While the efforts in this connection have not been attended with any degree of success, so far as the immediate scope of the problem is concerned, nevertheless it has led to a careful study of all the work thus far done upon the color of salts in solution. Results obtained in the case of iron salts by myself and others, and particularly those reported by Vernon,[1] have led to a conception concerning the origin of the color of such solutions which it is believed more satisfactorily accounts for the observed facts than any theory in its present shape.

In this connection it may be well to state that this article is written in no critical spirit, whatever, of the views of others; and I desire to say especially in regard to the work and theoretical conclusions of Vernon, who has contributed far more in the way of experiment upon this subject than any one else, that, while I beg to differ with him concerning his conclusions, I recognize that his experimental work has contributed far more to the ultimate solution of this problem than all speculation ever has or can.

As a result of his investigations he has arrived at the following important conclusions:

1. "Almost all the solutions of the thirty-five colored salts examined show considerable decrease in color-effect on dilution, due in all probability to dissociation taking place. The only exceptions are certain chromium derivatives, the color of whose solutions, on gradual dilution, either remains constant or increases

[1] Chem. News **66**, 104 *et seq.*

slightly. When their solutions are suddenly diluted different color-values are obtained. Potassium-permanganate solution only shows a very slight decrease in color on dilution. Taken as a whole, ferric salts show the greatest decrease in color-effect on dilution of their solutions, then cobalt salts, then uranium salts, and then nickel and cupric salts. Generally, also, organic salts show the most decrease of color on dilution, chlorides less, nitrates still less, and sulphates the least."

2. "All solutions of salts, with the exception of those of certain chromium derivatives and perhaps potassium permanganate, increase considerably in color-effect on being heated. The amount of color-increase depends on (1) the nature of the base of the salt, ferric solutions being most affected by temperature, then those of cobalt and uranium, and then those of copper and nickel; (2) on the nature of the acid radicle, chlorides being most affected, nitrates next, and sulphates least; (3) on the degree of dilution of the solution, sulphates being most affected in their decinormal solutions and least in the centinormal, whilst the chlorides are most affected in their normal solutions and least in their centinormal. The results obtained for the effect of temperature on the colors of salt-solutions are without exception in favor of the hydrate theory of the nature of solution."

3. "On comparing solutions of different salts together as to color-effect, it is found that the values obtained bear considerable resemblance to the amounts of decrease of color the solutions undergo on dilution, organic salts possessing the greatest color-effect, chlorides a less effect, sulphates and nitrates a still smaller color-effect. The results obtained, as a whole, indicate that dissociation takes place in solutions, on the one hand, and hydrates are formed on the other, so it would seem that salts exist in solution in both these conditions at the same time."

In view of these conclusions it might be well to compare the statements made by Ostwald,[1] in the treatise above referred to, concerning the color of salts in solutions, the more essential paragraphs being here quoted in full:

"The color of solutions is a property which is generally altogether constitutive, but for solutions of salts this property is additive. This result might be expected from the considerations which led to the supposition that the ions of a salt in solution exist

[1] Ostwald's "Solutions," pp. 268–9.

independently one of the other; the fulfilment of this expectation is, in turn, a very strong proof of the accuracy of the supposition.

"The colors of salt-solutions are essentially the colors of parts of molecules or ions contained therein, and all salt-solutions which contain a certain ion must exhibit the characteristic color of that ion. Should the expected color not appear, we may conclude that the corresponding ion is absent."

"The red color of dilute solutions of cobalt salts, for instance, indicates the presence of cobalt ions. The sulphate, nitrate, chloride, etc., have the same color in solution; the color is independent of the nature of the negative ions. If one of these solutions is boiled with an excess of potassium cyanide it is decolorized, *and the colorless solution no longer shows the reactions of cobalt.* The compound potassium cobalticyanide, $K_3Co(CN)_6$, has been formed; the ions of this compound are $3K$ and $Co(CN)_6$; free cobalt ions are no longer present. The green color of a solution of a nickel salt is changed, under the same conditions, to yellow, which shows that the nickel ions have entered into combination. If the foregoing statement is correct, the intensity of the coloration of those salts whose ions are colored must be proportional to the quantity of these ions, supposing that the part of the salt which is not separated into ions is itself colorless. An experimental examination of this question would not present special difficulties, but it has not been carried out as yet."

The facts observed by Vernon seem to be somewhat at variance with Ostwald's hypothesis, particularly with that part of it which supposes that the intensity of the color of those salts which are themselves colorless, but whose ions alone are colored, is proportional to the quantity of those ions, and therefore, in terms of the dissociation hypothesis, to the dilution. On the other hand, the explanation offered by Vernon, and that too in terms of the dissociation hypothesis given in the above, seems at variance with one of the fundamental assumptions of Ostwald's hypothesis, *viz.* that the ions of a colored salt are themselves colored. According to Vernon, the decrease in the color of salt-solutions on dilution is due to the dissociation of the salt into its ions. He is therefore forced to assume that these ions are themselves *colorless*, whereas the salt *per se* is the colored substance. Hence the more a given solution is diluted, the more and more it dissociates into colorless ions and the more and more it loses its original

color. To take a special example, he says, " If a dilute solution of a colored salt—as copper sulphate, for instance—contains less molecules of copper sulphate as such than a more concentrated solution, owing to the dissociation of the salt into its ions Cu and SO_4, it follows, if no other influences are at work, that with equal quantities of the salt present in each solution, the color of the dilute solution must be lighter than that of the more concentrated solution; and that, too, in proportion to the amount of copper-sulphate molecules dissociated into their ions." [1]

He seems to ignore the fact that anhydrous copper sulphate, in which probably there is no dissociation, is white; whereas it is only the hydrated varieties of this substance and its solution which are colored. In this connection it might be well to cite the view recently advocated by Linebarger,[2] to the effect that the blue color of the hydrated crystalline varieties of copper sulphate is itself evidence that even in the solid state, when combined with water of crystallization, copper sulphate has undergone dissociation. The fact certainly remains that the hydrated varieties of copper sulphate and the solutions of this compound show a marked increase in color over that of the anhydrous compound.

The development of this color by means of water would seem to be due either to the mere union of water with the molecule of copper sulphate, or else to a dissociating or decomposing action, or both, which it exerts, by virtue of which new substances are produced, one or all of which are blue in color. Regarding the first of these views, it may be said that it is difficult to conceive how the mere union of a colorless salt with its water of crystallization would produce blue or any other color; on the other hand, if the color be produced by the dissociating action of water simply, by virtue of which the salt is separated into its ions, one of which is colored, then it is equally difficult to conceive that this process should in the end make the solution lighter instead of increasing the depth or intensity of the color. As a matter of fact the dissociation theory alone seems unable to grapple with these curious facts. Vernon himself was not slow to recognize this difficulty. At the close of the second part of his communication[3] he says: " The changes in the color-effect of solutions of salts on dilution are evidently due to more than one cause. As will be shown, the formation of hydrates will account for them in part.

[1] Chem. News **66**, 104. [2] This Journal **14**, 604. [3] Chem. News **66**, 115.

They cannot be wholly accounted for in this way, however. Electrolytic dissociation seems the only ground left on which an explanation is possible." Again, at the close of the communication[1] he goes on to say that "The study of the colorimetric relations of solutions of salts at various dilutions and temperatures has thus been shown to give support to the electrolytic dissociation theory on the one hand, and to the hydrate theory upon the other. . . . It is hoped that these experiments may be taken to indicate the possibility of both of these theories being correct."

The fact that solutions of colored salts become lighter on dilution is not the only one at variance with the dissociation theory as enunciated by Ostwald.[2] There are still others. For example, salts of the same metal are known which possess two distinctly different tints when in solution. The salts of copper furnish an excellent illustration of this fact, and may be divided, according to their color, into at least two, perhaps three, classes: those which are blue, those which are green, and those possessing both of these colors, *viz.* bluish-green. These facts concerning the color of copper salts are so well known that it is scarcely necessary to give the following illustrative examples.

TABLE I.—*Copper Salts, arranged according to color.*

Blue.	Bluish-green.	Green.
Copper sulphate.	Copper chloride.	Copper isothionate.
" parachlorsulphobenzoate.	" ethoxyethanesulphonate.	" capronate.
" formate.		" N. heptylate.
" glycollate.		" N. caprylate.
" lactate.		" N. valerate.
" phthalate.		" propionate.
		" N. butyrate.
		" methylparanitrosulphobenzoate.[3]
		" ethylparanitrosulphobenzoate.

The blue or greenish-blue tint which copper chloride assumes in solution at various dilutions and temperatures is to be explained, according to the advocates of the dissociation theory, upon the

[1] Chem. News **66**, 153. [2] Ostwald: "Solutions," p. 268 *et seq.*

[3] Of the above salts, which in the solid state are described as having a greenish-blue or a greenish tint, the following at least have been found to give these same tints in solution: Copper chloride, copper N. butyrate, copper methylparanitrosulphobenzoate, copper ethylparanitrosulphobenzoate.

supposition that the greenish tints sometimes observable are due to a mixture of the blue ions of the dissociated portion of the salt with the yellow undissociated molecules.

While, perhaps, this explanation is in keeping with the facts observed in the particular case of copper chloride, it will not suffice to explain the green color of solutions of certain other copper salts. Two of these salts, *i. e.* copper methylparanitrosulphobenzoate, $\left(C_6H_3\begin{cases}COOCH_3\\SO_2O-\\NO_2\end{cases}\right)_2Cu + 8H_2O$, and copper ethylparanitrosulphobenzoate, $\left(C_6H_3\begin{cases}COOC_2H_5\\SO_2O-\\NO_2\end{cases}\right)_2Cu + H_2O$ (?) have come under my own observation,[1] and doubtless many others exist whose solutions are *green* in color; and yet these same salts when completely dehydrated are *white*. Plainly the green color observed in these cases cannot be due, as has been claimed in the case of copper chloride, to a mixture of the blue ions of copper with the undissociated portion of the salt. The undissociated portion of the salt is in this case white, and were it to find itself admixed with blue ions, it would in all probability simply tend to lighten the blue color. And again, upon the supposition that in the solution of this salt we have only the hydrated varieties together with blue ions, then we should expect to find the color of the solution a mixture of green and blue, or bluish-green. As a matter of fact, however, no such color is observable, the salt itself is a pale pearly green, and its solutions are pure green in color also. It is a green without a single tinge of blue about it, even at great dilutions.

In the light of these facts therefore, and upon the supposition that a salt in solution dissociates more or less completely into its ions, the one or the other conclusion would seem to be justified: either the ions themselves must be of different colors, or there are yet other forces at work in the production of the color than those indicated by the theory of dissociation. If the metallic ions of those salt-solutions in which the color depends upon the metal, be atomic, as generally represented, then the conception that any one may be of different colors is scarcely tenable, and hence that view which supposes the color of a salt and of its solution to be produced by more than one cause becomes all the more probable.

[1] Author's Thesis, J. H. U., 1888.

Before entering into a discussion of this latter view it might be well to give in this connection the work upon iron nitrate in solution, inasmuch as, as was stated at the outset, the views concerning the production of the color of salt-solutions in general, and which are subsequently to be discussed, were first suggested by the study of solutions of this substance.

Concerning the compound ferric nitrate it may be said that it appears to exist in several modifications containing different amounts of water of crystallization. All of these crystalline varieties are colorless or, like iron alum, possessed of a slight lavender color. The commonest of these has the composition $Fe(NO_3)_3.9H_2O$, and was first prepared by Ordway[1] by dissolving the metal in nitric acid. It may be prepared very simply as follows: Pure metallic iron is dissolved in rather strong nitric acid (sp. gr. 1.29), and the liquid evaporated to the consistency of a thick syrup; this in turn is dissolved in concentrated nitric acid and the solution left to evaporate and crystallize in a cold place. It was found advantageous to make the substance in winter weather. The compound melts at 45° C. to a dark red-brown solution, which on cooling resolidifies to a white crystalline substance. When dissolved in a small quantity of water, in which it dissolves in nearly all proportions, it forms a deep red-brown solution which becomes lighter and lighter upon dilution. Many attempts were made to determine the extent of the dissociation and decomposition by means of water and the resulting formation of iron hydroxide in the solution, by comparison of the color of the solution obtained at different dilutions with that of a standard solution of the same substance in which the quantity of iron hydroxide had been accurately determined by other methods. The attempt was also made to determine the extent of this decomposition by means of a standard solution of dialysed iron. Both of these attempts, however, resulted in failure, for the reason that the colors of many of these solutions were not comparable among themselves or with the standard solution, in consequence of a marked difference in tint. For example, at moderate dilution—such as normal and $\frac{1}{10}$-normal—the colors of the solutions of iron nitrate and the standards with which they were compared were nearly or quite the same; as the dilution increased, however, the solutions of iron nitrate took on a distinctly yellow tint, which was not present in

[1] Am. J. Sci. [2], **40**, 325.

the dilute solutions of dialysed iron, nor in the more concentrated solutions of iron nitrate used as a standard.

For example, a dilute solution of iron nitrate, so far as its brownish tint is concerned, may be exactly simulated by a dilute solution of dialysed iron, and yet the solution of the latter will not have the yellow tint of the former, nor will it have the same depth and fullness of color.

As stated above, in consequence of these marked dissimilarities of color, the attempt to measure colorimetrically the decomposition of iron nitrate by water was abandoned; nevertheless, the work in this connection revealed some interesting likenesses and differences among iron salts, and suggested some few thoughts concerning the color of salt-solutions in general.

With regard to solutions of ferric salts it may be observed:

(1) In concentrated solutions they all possess a distinct deep-red color.

(2) Concentrated solutions of all ferric salts pass on dilution from deep-red to brown and from brown to light yellow.

With regard to the first of these conclusions it may be said that the solutions of all ferric salts are more like a solution of ferric sulphocyanide than is generally supposed, and that the latter has many properties strictly in common with other ferric salts. The solutions of certain of the soluble ferric salts of the organic acids are especially very much like a solution of ferric sulphocyanide in color. Ferric acetate, for example, in solution in water and acetic acid, possesses such a deep-red color that, doubtless, solutions of this salt and of the sulphocyanide might be prepared so nearly alike in color as to be indistinguishable the one from the other. In support of the second of the above propositions, it has been observed that even the sulphocyanide assumes upon large dilution the same brown or yellow tint observable in the case of other ferric salts. It is very doubtful if the complete explanation of these interesting phenomena has ever been given. Wiedeman[1] has shown that a solution of iron alum conducts itself as though the free base and the free acid were present in its solution. The observations of Lea[2] support the same conclusion. It has been shown, further, by the advocates of the dissociation theory, that weak ions in general tend to react with the water, which has caused the dissociation, to produce new compounds. When ferric

[1] Ann. der Phys. Pogg. **126**, 1; **135**, 177. [2] Am. J. Sci. **45**, 478.

salts dissolve in water, for example, the iron ion Fe‴ being one of the weakest would take up the hydroxyl from three parts of water to form hydroxide of iron, which would remain in the solution in the colloidal state, while the resulting hydrogen would unite with the anion $(NO_3)_3$ to form free nitric acid.[1]

It will be observed that none of these facts and explanations seem capable of accounting for the differences in color observable in concentrated and dilute solutions of ferric salts.

Of the colloidal modifications of iron hydroxide, two have already been isolated, one brown in color, the other yellow. Upon the assumption of the existence of still another variety of colloidal iron oxide, red in color, it would seem that every fact concerning the changes in the color of ferric salt-solutions might readily be explained somewhat as follows:

When a colorless ferric salt dissolves in a small quantity of water it partially dissociates into colorless ions of iron and an acid residue. The ions of iron at once react with a certain portion of the water present to form iron oxide or hydroxide, red in color, and free nitric acid. As the dilution proceeds it may not be unreasonable to suppose that not only more dissociation of the iron salt takes place, but that also a portion of the iron oxide, or hydroxide already produced becomes so greatly hydrated as to produce a quantity of the yellow hydroxide, which mixing with the red variety gives the reddish-brown modification commonly existing in solutions of iron salts; and, finally, as the dilution becomes very great, not only would the dissociation reach its maximum, but also the hydration of the hydroxide produced, until at last only the yellow variety of the hydroxide remained in solution. It would thus appear that all facts concerning the colors of ferric salts in solution, and the changes in color which these same salts undergo by alterations in the quantity of solvent and physical conditions, could be correctly interpreted upon the assumption of the existence and formation in solution, of a red, hydrated oxide of iron, soluble in water.

Concerning this assumptiom it may be said that the fact that such a body has never yet been isolated is no proof of its non-existence; and, further, it has doubtless struck every one who has ever given the matter any attention, that were it possible to dissolve the purplish-red varieties of hematite in a neutral solvent,

[1] Oswald's *Lehrbuch*, 2, 794.

such as water, its solution would doubtless be of a deep blood-red color. There are several dyestuffs, dissolving in water with the production of a deep-red solution, which in their solid state are not unlike the purer varieties of hematite in appearance. The change which very dilute and yellow-colored solutions of ferric salts undergo on heating is in harmony with the views enunciated above. Such a change is attended with the production of a deeply colored red-brown solution. According to this hypothesis, such a change would signify that the greatly hydrated yellow variety of the hydroxide had lost a large portion of its water of hydration in consequence of the heat, and had therefore given rise to the less hydrated, red-brown modification. This view is strengthened by the fact that copper hydroxide loses its water on being gently heated, even in the presence and in contact with a thousand times the quantity of water necessary to form it; and by the fact that all hydrates, crystalline and amorphous, part with their water of hydration on being heated.

The decoloration of certain ferric salts, for example the sulphate and the nitrate, by means of strong mineral acids, particularly nitric acid, is a fact so well known that it is taken advantage of in one of the most reliable methods of volumetric analysis. When strong nitric acid in sufficient quantity is added to a solution of iron nitrate it becomes as clear and colorless as water; upon standing for a time, however, it assumes a very pale yellow color, and then resembles precisely a very dilute solution of iron nitrate alone.

Again, the explanation of this phenomenon is furnished by the above hypothesis: when nitric acid is added to a colored solution of iron nitrate it at once combines with the hydroxide of iron in the solution to form iron nitrate, which in the undissociated condition is colorless. In the course of time, however, the newly formed nitrate will undergo a slight dissociation, and as a result there will again be formed a small quantity of iron hydroxide. This now, finding itself in a relatively large quantity of water, is converted into the yellow hydroxide peculiar to very dilute solutions of ferric salts.

It is believed that these considerations apply with equal force to the explanation of the facts observed in the case of the colored solutions of other salts.

For example, as above cited, the following facts have been observed concerning the color of various copper salts in water:

1. The color of copper salts in solution is either blue or green or a mixture of these two colors.

2. These solutions become lighter upon dilution.

3. These solutions become darker on heating.

4. That of four of these salts—*viz.*, the sulphate, nitrate, chloride and acetate—the acetate, at corresponding dilutions, is much the darkest and strongest in color of the four. The acetate was found by Vernon[1] to be about eight times more densely colored, whereas between the chloride, nitrate and sulphate the difference in color was but slight.

Now, on the supposition that two soluble hydroxides of copper exist in solutions, we have a ready explanation of the first of the above general conclusions, *viz.*, that these solutions are either *green* or *blue*.

Secondly, the hydration of each of these hydroxides upon dilution of the solution, would certainly account for the fact of their becoming lighter in color on dilution.

Thirdly, that these solutions become darker on being heated is, in the light of this hypothesis, to be accounted for upon the supposition that these highly hydrated and lighter hydroxides lose some of their water upon being heated.

And, lastly, the fact that the acetate forms a much more deeply colored solution than either of the other salts, is not only explicable by, but furnishes strong support for, this hypothesis. We may suppose that, as with other salts, the copper acetate dissociates; the acet ion, however, is so weak that it very readily unites with the water present to form acetic acid. The setting free of the hydrogen of the water, however, and the formation of acetic acid involve a corresponding formation of the base, and that, too, in larger quantities than it is formed in the case of stronger acids; and hence, owing to the larger quantity of copper hydroxide, the solution of copper acetate is darker than either the chloride or the sulphate.

In other words, according to this hypothesis, whatever changes occur in the molecule of copper acetate when it goes into solution, these same changes take place with the other salts of copper, only to a greater or a less extent, depending upon the nature of the acid with which the metal finds itself in combination: and all of these changes, by virtue of which a salt produces a colored solu-

[1] Chem. News **66**, 152.

tion, are alike in kind and differ only in degree. For example, if we have in the case of copper acetate not only a dissociation but also a subsequent and dependent formation of the base copper hydroxide; so in copper chloride or sulphate we have not only a dissociation of the molecule into its ions, but also a subsequent decomposition of a part of the water present by means of one or both of these ions, whereby not only ions of copper and acid residues find themselves present in the solution, but also some free base and some free acid. It is upon this decomposition and its extent that the kind of color and also its intensity depend in the case of salts in solution. The only essential difference between the color of a solution of copper acetate and that of a solution of the sulphate would depend upon the extent to which one or the other of these processes had been carried. In the case of copper acetate the dissociation is small, whereas the conversion of copper ions into the hydroxide is relatively great; on the other hand the dissociation in the sulphate is large, and the conversion of copper ions into the hydroxide is relatively very small.

It would seem that this view that all salts which give colored solutions have not only been dissociated, but partially decomposed, by water, derives a certain support from the fact that of the many salts forming colored solutions but few, if any, are neutral. Most of them are acid in reaction.

According to the advocates of the dissociation theory, a solution of potassium carbonate is alkaline for the reason that a base and an acid are both formed in solution, and of these two substances the base is much the stronger and hence gives to the solution its own reaction. It would seem that the converse of this ought to be true, *viz.* that the non-neutrality of a solution of a substance shows that not only has dissociation taken place, but also the subsequent formation of the acid and base from the salt. The marked acidity of a solution of copper sulphate, for example, ought to show that this salt has been decomposed by water, giving rise to a small quantity of the base $Cu(OH)_2$ and the acid H_2SO_4. Of these two substances, however, the sulphuric acid is the stronger, and hence the acidity of the solution; on the other hand, the acid being colorless and the base blue, the latter manifests its existence by imparting to the solution its characteristic color.

Again, in support of the view that we really have free bases in the solutions of colored salts may be cited the fact that many if

not all of these metals tend to form basic salts, in which the presence of the hydroxide has been proven beyond a doubt; and it is interesting to note in this connection that in the case of copper salts, those which are basic have, as a rule, a green color, whereas the normal ones are blue. It is certainly difficult to see how these basic salts could have been formed from a solution of the normal salts, if prior to their formation the hydroxide in some form or other had not existed in the solution.

It may be argued that this view concerning the existence of the free acid and base in solutions of colored salts is inadmissible, on the ground that such solutions show none of the general properties of an acid or an alkali, such as characteristic taste, smell, etc. To this it may be replied, that the quantity of an acid or base, either directly or indirectly concerned in the production of a color, may be altogether too small, and too much obscured by the properties of the salt as a whole, to be recognized by either of these senses. As a matter of fact it is well known that the quantity of an acid or of a base which will affect the color of an indicator is as a rule entirely beyond the reach of either taste or smell.

Looked at from another standpoint, it is very much to be doubted if there is anything like *absolute neutrality* among any but a few of the salts of very powerful metals with very strong acids. As stated above, most of the colored salts are acid even to our ordinary indicators, such as litmus and phenolphthalein, and it is certainly much to be doubted if any of these would be found *neutral* if judged by some of the newer standards.[1]

Again, it may be said in this connection that water in much of its conduct is very much like a weak acid; in view of which the formation of oxides and hydroxides from salts in solution is to be regarded after the manner of a partial double decomposition.

By way of conclusion, it may not be amiss to state again, succinctly and briefly, the objections which have been urged against the other hypotheses concerning the color of salts and their solutions, and to give an outline of the substitute which is herein proposed, and which has been discussed at length in the above.

First.—The dissociation theory alone seems incompetent to explain the following facts concerning the color of certain salts in solution:

(1). The solutions of different salts of the same metal may and do possess two or more distinct colors.

[1] This Journal **15**, 663.

(2). The color of salt-solutions, in the cold, grows lighter, or is less, on dilution.

Secondly.—The hydrate theory of solution also seems incapable of satisfactorily explaining the facts. For example, it is difficult to conceive how the mere addition of water of hydration should work so radical a change in the properties of a compound as to change a white substance to one having a blue or red color. It would rather seem that the water worked a deep-seated change in the compound, and so by its action brought out some latent property of the substance acted on.

In view of the fact that the two theories mentioned above do not satisfactorily account for many of the observed facts, the following hypothesis has been put forward, *viz.* that the color of a salt-solution is dependent not upon the color of the ion, but upon the color of the base or that of the acid, either or both of which may be colored; and further, that the base or the acid to which the color is due may possess, according to conditions at present unknown, two or more distinct colors. The argument is largely one of analogy. It has been proven in the case of ferric salts that at least two soluble, collodial, modifications of the hydroxide of iron exist; and that, while ferric salts in much of their conduct offer an extreme case, it is assumed that the differences between them and other salts are of degree rather than of kind. Hence, if two soluble hydroxides of iron have been isolated, there may be yet another of this element and two or more of any other metal whose salts are colored.

Again, the following facts have been or may be cited in support of the view that we really have the free acid and base in solutions of colored salts:

(1). Most of these salts, if not all, are acid in reaction.

(2). Most of them form basic salts readily.

(3). Water in many of its reactions may be regarded as an acid, and hence the formation of hydroxides in solution is similar to double decompositions.

(4). The many phenomena of the coloration of salt-solutions.

In other words, by far the greater number of facts pertaining to the color of salt-solutions, and the changes which they sometimes undergo are accounted for by this hypothesis. It is believed that it serves its purpose better than any which has yet been put forward concerning these interesting and beautiful phenomena; and

in a way it will serve that purpose well if it but directs our attention to the fact that the present theories concerning the formation of these colors are far from perfect, and points the way for further investigation in this interesting field.

STATE COLLEGE OF KENTUCKY, LEXINGTON, *February*, 1894.

RESEARCHES UPON THE PHENOMENA OF OXIDATION AND CHEMICAL PROPERTIES OF GASES.

BY FRANCIS C. PHILLIPS.

[*Continued from page* 277.]

Acetylene.

This hydrocarbon was prepared by the action of alcoholic potash upon ethylene dibromide.[1] The method of preparation proposed by Berthelot,[2] by causing a Bunsen burner to "strike back," although applicable for coal-gas, has not given satisfactory results when natural gas was used.

1.—*Reactions in Solution.*

Reagents.	Reactions.
Palladium chloride	Reddish-brown precipitate. No reduction occurs. Very sensitive.
Platinum chloride	Unchanged, cold or at 100°.
Gold chloride	Immediate reduction. Intensely black precipitate of gold. No carbon dioxide formed.
Gold chloride in excess of potash	No change, cold; trace of reduction at 100°.
Silver nitrate	White precipitate. Very delicate reaction.
Ammoniacal silver nitrate	White precipitate, which is so gelatinous that a 10-per cent. solution of silver nitrate becomes nearly solid, like boiled starch.
Iridium chloride	No change, cold; reduction after one week, or on boiling.

[1] See p. 181.

[2] Ann. chim. phys. [5] **10**, 365 (1877).

Rhodium chloride.....	Unchanged.
Potassium rutheniate.....	Very slow reduction.
Cerium dioxide in dilute sulphuric acid.	Slowly bleached.
Potassium permanganate.....	Turns brown at once.
Potassium permanganate in dilute sulphuric acid.	Quickly bleached.
Potassium permanganate crystals in concentrated sulphuric acid.	The gas is immediately oxidized to carbon dioxide.
Potassium bichromate acidulated with sulphuric acid.	The color is unchanged, cold or at 100°.
Osmic acid.....	Quickly reduced, turning black from precipitated metal.
Copper sulphate in neutral or ammoniacal solution.	Unchanged.
Ferric chloride.....	Decided reduction to ferrous chloride in twenty-four hours, cold.
Calcium hypobromite containing excess of lime-water.	Acetylene is slowly oxidized, yielding carbon dioxide, the lime-water becoming milky.
Hydrogen peroxide and lime-water..	The fluid remains clear.
Bismuth pentoxide in excess of caustic potash solution.	Unchanged.
Potassium ferricyanide	Unchanged.
Iodine dissolved in potassium-iodide solution.	Unchanged. The color is not bleached.
Yellow oxide of mercury.....	Unchanged in color.
Mercurous nitrate.....	White precipitate.
Cuprous chloride in ammonia.....	Deep-red precipitate, the well-known "copper acetylide."
Chromous sulphate.....	Is said to absorb acetylene.[1]
Mercuric chloride	White precipitate. Very delicate reaction.

2.—*Reactions at High Temperatures.*

Iodic acid in crystals was found to be reduced by acetylene at about 90°. In this reaction iodine vapors and carbon dioxide appeared. Aside from the experiments on oxidation by finely divided metals already detailed, no other reactions at high temperatures were tried.

Comments.—Ammoniacal cuprous chloride, the absorbent commonly recommended for acetylene, although a very delicate reagent for the recognition of the gas, is at the same time slow and its action is liable to be incomplete. A single bubble of the

[1] Roscoe and Schorlemmer: Vol. II, Pt. II, p. 160.

gas will cause a decided red precipitate, but acetylene may be passed slowly through a series of Woulfe bottles containing the ammoniacal cuprous-chloride solution and yet be very incompletely absorbed, so that it may still cause precipitation in the same reagent. The bright-red precipitate dissolves easily in hydrochloric acid, with evolution of acetylene on boiling. This affords a convenient and well-known method for the purification of the gas. Exposed to the air, however, the red compound changes to a deep brownish-black and becomes insoluble in acids. Consequently, in preparing and washing the red copper acetylide, with a view to its decomposition by hydrochloric acid which liberates the pure acetylene, great care is necessary to avoid exposure to the air.[1] According to Berthelot,[2] the copper compound is vinyl oxide in which copper has replaced hydrogen: $Cu_2:C:CH—O—CH:C:Cu_2$. According to Keiser, the copper and silver compounds are Cu_2C_2 and Ag_2C_2.

Silver nitrate is probably the most sensitive reagent tried. Moreover, as the silver compound does not appear to be susceptible to oxidation, it may be used in testing for acetylene in the presence of air or oxygen, while the copper compound, on account of its strong tendency to undergo oxidation, is far less easily recognized in the deeply colored copper solution. Potassium permanganate in concentrated sulphuric acid, calcium hypobromite and osmic acid are the only reagents which in the cold cause direct oxidation of acetylene to carbon dioxide. As an unsaturated hydrocarbon, its indifference towards iodine solution was somewhat unexpected in view of the avidity of isobutylene for iodine.[3]

The prompt reduction of gold chloride forms a singular contrast to the indifference of platinum chloride towards acetylene. The color of the gold when precipitated by acetylene (usually blue or blue-black) is quite different from the brownish-yellow color so often observed when gold salts are reduced. This difference in color of the precipitated gold is probably not due to rapidity of reduction.

Allylene.

This hydrocarbon was prepared from propylene bromide by the action of alcoholic potash. The gas resulting was washed by

[1] Keiser: This Journal **14**, 285 (1892). [2] Bull. Soc. chim. [2] **5**, 191 (1866).
[3] See page 370.

being passed through boiling alcoholic potash solution and absorbed by ammoniacal cuprous chloride. The yellow precipitate resulting was washed and afterwards decomposed by hydrochloric acid, allylene being then set free in a pure state.

1.—*Reactions in Solution.*

Reagents.	Reactions.
Palladium chloride	Dark-brown precipitate, which may be preserved without decomposition. Closely resembles the precipitate produced by acetylene.
Platinum chloride	Unchanged.
Gold chloride	Slowly reduced. The color of the precipitated gold is very dark.
Silver nitrate	A 10-per cent. solution quickly coagulates to a white, curdy mass. The precipitate dissolves on boiling or on addition of ammonia. A very delicate reaction.
Ammoniacal silver nitrate	Unchanged.
Iridium chloride	Unchanged in the cold, at 100° iridium is precipitated.
Rhodium chloride	Unchanged.
Potassium rutheniate	Slowly reduced. Black precipitation of metallic ruthenium.
Cerium dioxide dissolved in dilute sulphuric acid.	Unchanged.
Potassium permanganate	Quickly turns brown.
Potassium permanganate in dilute sulphuric acid.	Quickly bleached.
Potassium permanganate crystals in concentrated sulphuric acid.	Prompt oxidation to carbon dioxide.
Mercuric chloride	Dense white precipitate. Very delicate reaction.
Potassium bichromate acidulated with dilute sulphuric acid.	Unchanged in color.
Osmic acid	Reduced. Metallic osmium is deposited as a black powder.
Ferric chloride	Decided reduction to ferrous chloride.
Calcium hypobromite	Allylene is oxidized to carbon dioxide. The fluid grows milky.
Lime-water and hydrogen peroxide.	Unchanged.
Potassium ferricyanide	Unchanged.
Iodine dissolved in potassium-iodide solution.	Unchanged.
Cuprous chloride in excess of ammonia.	Canary-yellow precipitate, changing slightly to greenish-yellow on contact with air. Soluble in acids, with liberation of allylene.
Mercurous nitrate	White precipitate.

2.—*Reactions at High Temperatures.*

Experiments were tried in the reduction of certain metallic oxides, but the results are not of sufficient importance to be detailed here.

Comments.—The reactions of allylene closely resemble those of acetylene. As regards intensity, scarcely any difference can be found. The colors of the palladium compounds of acetylene and allylene do not differ materially. Towards ammoniacal cuprous chloride the two gases exhibit very characteristic differences as regards the color of the resulting compound. The copper allylide is easily soluble in dilute hydrochloric acid. Ammoniacal silver nitrate yields a gelatinous precipitate with acetylene, but is not changed by allylene. Oxidation of allylene to carbon dioxide, as in the case of acetylene, is not easily effected except by the most powerful oxidizing agents, such as calcium hypobromite or potassium permanganate in concentrated sulphuric acid. Although the allylene copper compound is rapidly formed in an ammoniacal cuprous-chloride solution, the absorption of the gas is singularly incomplete. Agitation with the solution is quite necessary in order to insure complete absorption. Wagner[1] has shown that the higher acetylenes, like the olefines, are converted by neutral potassium-permanganate solution into hydroxyl compounds.

The various classes of hydrocarbons of the fatty series possess in common a high resistance to destructive oxidation by oxidizing agents, yielding in some cases hydroxyl compounds, but rarely carbon dioxide. This is true also of benzene, which is changed by potassium permanganate into oxalic acid and formic acid.[2]

Sulphur Compounds.

Carbon Oxysulphide.

This gas was prepared by the method of Klason.[3] To a cold mixture of 290 cc. sulphuric acid and 400 cc. water, 50 cc. of a saturated solution of sulphocyanide of potassium was gradually added, the mixture being warmed to 30°. The gas was evolved in a steady stream and was purified by passage (1) through 20-per cent. potash solution, (2) through 25-per cent. solution of aniline in alcohol, (3) through broken ice.

[1] Ber. d. chem. Ges. **21**, 3343 (1888). [2] Bernthsen: p. 326.
[3] J. prakt. Chem. [2] **36**, 64 (1887); Ber. d. chem. Ges. **20**, Ref. 550.

Carbon oxysulphide was also prepared by the action of carbon disulphide on alumina at a high temperature.[1] The gas, if dry, may be preserved over mercury. Contact with water causes a change into carbon dioxide and hydrogen sulphide. Caustic soda solution is changed into a mixture of sodium sulphide and carbonate. The constant tendency to decomposition renders it impossible to preserve the gas over water without loss. In trying its reactions, it was found necessary to conduct the gas immediately before use into some substance specially adapted to absorb hydrogen sulphide. For the absorption of this gas Fresenius[2] recommends pumice saturated with copper-sulphate solution and dried. In a series of trials with this and other absorbents, precipitated oxide of mercury was found to answer best. Dampened absorbent cotton is coated with the yellow powder by rubbing with a large pestle. This preparation, used dry in a long glass tube, completely removes hydrogen sulphide, but exerts no action upon carbon oxysulphide.

I.—*Reactions in Solution.*

Reagents.	Reactions.
Palladium chloride	Prompt precipitation. Precipitate is brownish-black and flocculent.
Platinum chloride	Black precipitate.
Gold chloride	Rapidly darkens. An olive-brown precipitate collects.
Copper sulphate	Black precipitate, which forms very slowly.
Ammoniacal copper sulphate	Black precipitate, forming promptly.
Silver nitrate	Voluminous, brownish-black precipitate.
Ammoniacal silver nitrate	Prompt precipitation.
Cadmium chloride	Precipitation is slow and incomplete.
Cadmium chloride in excess of ammonia.	Rapid and complete precipitation; bright yellow.
Arsenious chloride	Yellow precipitate, forming very slowly.
Potassium permanganate acidulated by hydrochloric acid.	Rapidly bleached. The solution then precipitates barium chloride, so that oxidation to sulphuric acid has occurred. No separation of sulphur is observed.
Lead acetate	Black precipitate.
Bromine-water	Prompt oxidation to sulphuric acid. No sulphur is separated.

[1] Gautier: Compt. Rend. **107**, 911.

[2] Quant. Analyse, 6te Auflage.

Mercuric nitrate	Turns milky white and darkens gradually to black.
Nickel hydrate in water	Darkens slowly to black.
Ferric chloride	Decided but incomplete reduction to ferrous chloride.
Potassium ferricyanide	Traces of reduction to ferrocyanide.
Osmic acid	Rapidly reduced.
Potassium rutheniate	Rapidly blackened.
Cerium dioxide in dilute sulphuric acid.	Rapidly bleached.
Yellow oxide of mercury	These are all unchanged if dry. Sealed in a glass tube filled with the gas for two months, no change had occurred. If spread upon cotton, these substances may be used to remove sulphuretted hydrogen from a mixture of the two gases.
Litharge	
Precipitated carbonate of copper	
White lead	
Silver foil	Is unattacked if dry; under water it is quickly blackened.

Comments.—Carbon oxysulphide, by reason of its ready change in presence of water into hydrogen sulphide and carbon dioxide, gives, in the main, the reactions of hydrogen sulphide, so that by the reagents usually employed for the detection of the latter gas these two sulphur compounds are not distinguishable. In fact, towards ammoniacal cadmium-chloride solution, silver nitrate and palladium chloride, its reactions are characterized by somewhat greater promptness than in the case of hydrogen sulphide. It is to be noted that, should hydrogen sulphide and carbon oxysulphide occur in a gas mixture, the latter would, by ordinary analytical methods, be mistaken for the former, and equal volumes of the two gases would yield the same weight of the sulphides of silver, cadmium, copper, etc.

The principal metallic sulphides as usually formed by hydrogen sulphide could be, in many cases, more rapidly produced by carbon oxysulphide; and, so far as I have been able to observe the reactions, there is little or no tendency to separation of free sulphur such as is common in precipitations by hydrogen sulphide. The absorption of carbon oxysulphide in ammoniacal cadmium solution is so complete that on passing the gas through this solution none will escape unabsorbed to cause precipitation in a second solution. An analysis seemed desirable in the case of the silver compound obtained when carbon oxysulphide was passed through

a solution of ammoniacal silver nitrate, as the precipitate appeared much more flocculent and of a more brownish color than ordinary, precipitated silver sulphide. Accordingly, determinations of silver and of sulphur were made with the following results:

	Calculated for Ag_2S.	Found. (1)	(2)
Ag	87.06	91.15	90.95
S	12.94	8.70	8.75
	100.00	99.85	99.70

Hence the compound consisted of silver sulphide, with a small quantity of silver thrown down by the carbon monoxide present in the gas.

Yellow mercuric oxide forms an excellent means of separation of the two gases, and after the removal of the hydrogen sulphide by this reagent used in a dry state, the production of a precipitate in ammoniacal cadmium-chloride solution would indicate that this cadmium sulphide has been caused by carbon oxysulphide.

The presence of a little carbon monoxide in the carbon oxysulphide made from potassium sulphocyanate and sulphuric acid, is liable to mislead in the reaction towards palladium chloride, causing a black precipitate of palladium resembling the sulphide.

Methyl Hydrosulphide, CH_3SH.

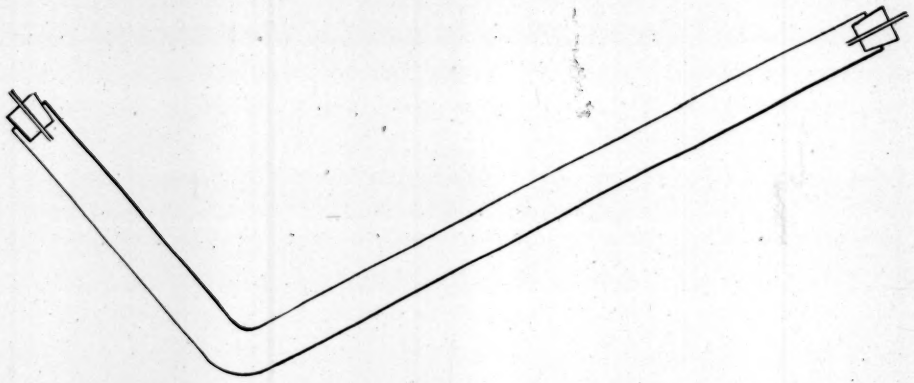
This gas may be produced by several typical reactions:

(1) When methyl chloride (bromide or iodide) is heated with potassium hydrosulphide in alcoholic solution, the reaction being

$$CH_3Cl + KSH = KCl + CH_3SH.$$

Methyl chloride gas was conducted into a boiling alcoholic solution of potassium hydrosulphide contained in a tube of the shape here shown.

The long limb of the tube (length, thirty inches) was connected with a reversed condenser and was heated over a small flame. The gas as it escaped was passed through a long glass tube containing cotton coated with red oxide of mercury, which absorbs any possible traces of hydrogen sulphide and some of the mercaptan. The gas was passed through broken ice. As the reaction above mentioned is rather incomplete, the gas contains much unaltered methyl chloride. The same is true when the bromide and iodide



are used. Methyl chloride is the best suited to the purpose, since it may be conducted into the liquid as a *gas*. The iodide, being a very volatile liquid, is not easily added without danger of tumultuous boiling. Formation of difficultly soluble potassium chloride or iodide causes clogging and greatly interferes with the process, even when large delivery-tubes are used.

(2) Methyl sodium sulphate and potassium hydrosulphide, on being brought together and warmed, yield the following reaction:

$$NaCH_3SO_4 + KHS = KNaSO_4 + CH_3SH.$$

The reaction may be carried out in aqueous solution by the very excellent method of Klason.[1] He directs as follows: 800 grams potassium hydroxide are dissolved in water; the solution is saturated by sulphuretted hydrogen. It is placed in a large flask and sodium methylsulphate, made from 500 cc. methyl alcohol, added in small portions. On gently warming, a mixture of the vapors of methyl sulphide and hydrosulphide is evolved. The vapors are passed through an empty bottle and then into a second bottle containing soda solution, which should be cooled. The methyl hydrosulphide is completely absorbed by the soda, forming sodium methyl sulphide, or mercaptide, $NaCH_3S$. The sodium mercaptide so produced is very stable. Methyl sulphide condenses to a liquid which floats on the soda solution, but does not combine with the soda. A separation is therefore easily effected. The methyl sulphide may be driven off by warming the bottle containing the soda solution, the mercaptide being unaffected by the heat. The methyl sulphide may thus be used in vapor-form to produce its reactions. After expulsion of the methyl sulphide, the soda solution may be placed in a flask and decomposed by dilute sulphuric acid, and methyl hydrosulphide then expelled as a gas. Some lead acetate is added to the solution in order to bind sulphuretted hydrogen during the decomposition of the sodium mercaptide by acid.

Klason advises a further purification; but, by the process described, the two sulphur compounds may be obtained of sufficient purity for the study of their reactions. Methyl hydrosulphide is a gas above 6° C. (Klason). It is remarkable for its penetrating odor, which adheres most tenaciously to all surfaces, glass not excepted, for months. All work with the gas should be

[1] Ber. d. chem. Ges. **20**, 3407 (1887).

done out of doors. It is somewhat soluble in water, to which it imparts its properties.

The compounds produced by the action of methyl hydrosulphide upon metallic oxides are the true mercaptides. Typical of these is the mercury mercaptide, which results as follows:

$$HgO + 2CH_3SH = (CH_3S)_2Hg + H_2O.$$

The yellow lead compound has the formula $(CH_3S)_2Pb$; the copper compound, CH_3SCu; the silver compound $(CH_3S)Ag$.[1] Methyl hydrosulphide combines also with metallic chlorides:

$$HgCl_2 + CH_3SH = CH_3SHgCl + HCl.$$

According to this reaction, numerous metallic compounds are formed. These compounds change more or less readily, on exposure to air, into metallic sulphides (Klason).

Reactions.

The vapor was caused to bubble through various solutions with the following results:

Reagents.	Reactions.
Palladium chloride	Cinnamon-colored, flocculent precipitate in strong or weak solutions. Insoluble in hydrochloric acid, nitric acid, sulphuric acid, *aqua regia*, ammonia and caustic soda, in the cold or at 100°. Extremely delicate reaction.
Platinum chloride	Yellowish-brown, flocculent precipitate in dilute or concentrated solution. Insoluble in the strong acids and alkalies, and in this respect similar to the palladium compound.
Iridium chloride	Yellow precipitate, resembling in appearance the platinum compound.
Gold chloride	Light yellow, very voluminous precipitate, changing gradually to white as the passage of the gas is continued, and finally redissolving to a clear solution.
Mercuric chloride	White, flocculent precipitate. Darkens slightly on exposure to air and light. Extremely delicate reaction.

[1] See Klason: *loc. cit.*; and Richter: Org. Chem., trans. by Smith, p. 143.

Copper sulphate	Straw-yellow precipitate, insoluble in ammonia. Darkens rapidly. Soluble in hydrochloric acid. The hydrochloric-acid solution of the precipitate contains cuprous chloride.
Ammoniacal copper sulphate	Yellow precipitate like the preceding. Soluble in hydrochloric acid to cuprous salt. Rapidly darkens.
Cuprous chloride	White, flocculent precipitate, changing to crystalline needles. More stable than the preceding compound.
Silver nitrate	Yellow precipitate, resembling in appearance the copper compound. Insoluble in ammonia. Rapidly blackens.
Ammoniacal silver nitrate	Yellow precipitate, similar in appearance and properties to the preceding.
Ammoniacal cadmium chloride	White precipitate in flocculent masses, somewhat soluble in the reagent and in water. Permanent, if protected from the air. By oxidation is converted readily, in the cold, into yellow cadmium sulphide.
Arsenious chloride in dilute hydrochloric acid.	The fluid grows milky from floating oil drops, which gradually collect as a very heavy oil at bottom.
Zinc sulphate in excess of caustic soda solution.	Unchanged.
Potassium permanganate, 6-per cent. solution acidulated by hydrochloric acid.	Rapidly bleached. Becomes heated from the intensity of the reaction. No sulphuric acid is produced.
Lead acetate.	Straw-yellow precipitate, insoluble in acids and alkalies. Rapidly blackens.
Potassium bichromate acidulated by hydrochloric acid.	Promptly reduced to green chromic chloride. No sulphuric acid is produced.
Bromine-water	Rapidly bleached. No sulphuric acid is produced.
Mercurous nitrate	Grayish-black precipitate.
Bismuth nitrate	Slowly forming black precipitate
Nickel hydroxide in water	Slowly blackens.

Ferric hydroxide in water.....	Unchanged.
Yellow oxide of mercury.....	Turns slowly gray and finally black.
Ferric chloride.....	Rapidly reduced to ferrous chloride. No sulphuric acid is formed and no sulphur liberated.
Potassium ferricyanide	Reduced to ferrocyanide.
Osmic acid	Rapidly blackened.
Potassium rutheniate.....	Extremely slow and incomplete reduction.
Hydrogen peroxide.....	No oxidation to sulphuric acid occurs.
Cerium dioxide in dilute sulphuric acid.	Quickly bleached.
Litharge and white lead.....	Quickly changed, yielding a voluminous yellow powder.
Copper carbonate	The resulting mercaptide is similar in appearance to that obtained in the preceding reaction. The mercaptides of lead and copper are very stable.
Silver foil	Is not changed, dry or in water. After three months the silver appeared slightly darkened in color.

Comments.—In the remarkable diversity of its reactions, methyl hydrosulphide probably excels every other known gas. The stability of many of its metallic compounds is often nearly as great as that of the corresponding sulphides. The reagents employed include many substances of high oxidizing power. It was not possible, however, to detect in any case a trace of sulphuric acid. Under the influence of oxidizing agents, the tendency of the mercaptans is to produce the sulphonic acids.

$$CH_3SH + O_3 = CH_3SO_3H.$$

Hence the failure to form sulphuric acid. The following experiment illustrates the remarkable stability of methyl hydrosulphide:

The gas was passed in slow stream through a glass combustion-tube containing a fused mixture of sodium carbonate and potassium bichromate, but no sodium sulphate was produced. Moreover, the gas escaping from the tube possessed the characteristic odor of the mercaptan. The same experiment was tried with a mixture of sodium carbonate and sodium nitrate with a similar result. On account of its numerous reactions towards the various metallic salts, a separation of methyl hydrosulphide and sulphur-

etted hydrogen is a difficult matter. As it acts slowly and incompletely upon yellow mercuric oxide, this substance may be used to absorb sulphuretted hydrogen. Although methyl hydrosulphide attacks and combines with the mercuric oxide, sulphuretted hydrogen gradually expels it, the yellow color gradually changing to black, owing to the formation of sulphide of mercury. The yellow copper compound changes into copper sulphide. The same is true of the yellow compounds of lead and silver and the white cadmium compound. This change into sulphide is in every case promoted by exposure to air, especially in presence of ammonia. In an aqueous solution of methyl hydrosulphide containing neither acids nor alkalies, the various compounds are more stable.

The mercaptides are easily produced in many cases by the action of a solution of the mercaptan in water upon the oxides, hydroxides or carbonates of the metals, and when so formed they are easily preserved unchanged.

It is of importance to note that sulphuretted hydrogen expels methyl hydrosulphide from many of its metallic compounds. The reactions of the latter towards gold chloride and arsenious chloride are especially remarkable. In the former case the production of a precipitate, gradually changing from yellow to white and finally disappearing, distinguishes this gas from sulphuretted hydrogen. The formation of an oily liquid insoluble in water, in the case of arsenious chloride, also serves to distinguish between the two gases.

Methyl Sulphide.

This compound may be prepared by the action of methyl iodide (or, preferably, methyl chloride) upon potassium sulphide in alcoholic solution. Gaseous methyl chloride may be led into an alcoholic solution of potassium sulphide contained in a flask heated over a water-bath and connected with a reversed condenser. The vapor of methyl sulphide thus formed may be freed from sulphuretted hydrogen by oxide of mercury or by passage through warm soda-solution.

In the process of Klason, already described, methyl sulphide is produced simultaneously with the hydrosulphide. The process yields, in fact, a larger proportion of the former than of the latter. It may be readily separated, as already stated, by means of soda-

solution, which absorbs and combines with the mercaptan but exerts no action upon the sulphide. On warming the soda-solution, therefore, the sulphide, condensed and floating upon its surface, may be expelled in vapor-form. In the following experiments methyl sulphide was used, prepared by the action of methyl chloride upon potassium sulphide and also by the method of Klason. Methyl sulphide is a colorless liquid, boiling at 37° C.

The compound formed by mercuric chloride with methyl sulphide is $(CH_3)_2SHgCl_2$. The yellow precipitate produced in platinum-chloride solution is $PtS_2(CH_3)_4Cl_4$. On standing or on warming, the powder changes to a crystalline, isomeric form.[1]

Bromine combines directly with methyl sulphide, yielding a crystallizable, volatile compound $(CH_3)_2SBr_2$. Oxidation by nitric acid converts methyl sulphide into the compounds $(CH_3)_2SO$ and $(CH_3)_2SO_2$; as already stated, it appears to be impossible to oxidize the thio-ether to sulphuric acid by reagents in solution.[2]

Reactions.

In the following experiments the vapor was caused to pass into the various solutions.

Reagents.	Reactions.
Palladium chloride.....	No change in highly dilute solution. In a 2-per cent. solution of palladium chloride, an orange-colored, pulverulent precipitate occurs, soluble on boiling. As the solution cools, the substance is redeposited in beautiful, orange-colored crystals. These crystals are apparently monoclinic and, although none were obtained sufficiently large for measurement, they resemble strongly the usual forms of selenite.
Platinum chloride.....	Precipitate of a lighter yellow color than the preceding. Somewhat soluble on heating, but less so than the palladium compound. The precipitate becomes distinctly crystalline on standing.

[1] For an important discussion of this and other alkyl-sulphide compounds see Enebuske: *J. prakt. Chem.* [2] **38**, 358 (1888).

[2] See Richter: Organic Chemistry, trans. by Smith.

Gold chloride	Yellow precipitate, which becomes white and finally redissolves on continuing to pass the vapor through the solution.
Mercuric chloride	White precipitate. Very delicate reaction. When highly magnified the precipitate is seen to consist of transparent crystals, apparently monoclinic.
Copper sulphate	Unchanged.
Ammoniacal copper sulphate	Unchanged.
Silver nitrate	Turns brown, but little or no precipitation occurs.
Ammoniacal silver nitrate	Unchanged.
Cadmium chloride	Unchanged.
Ammoniacal cadmium chloride	Very slight precipitation, which dissolves in the reagent or in acid.
Arsenious chloride	Unchanged.
Potassium permanganate, acidulated by hydrochloric acid.	Rapidly bleached. No sulphuric acid is formed.
Lead acetate	Unchanged.
Bromine-water	Rapidly bleached. On evaporation, a crystalline residue results. The substance is volatile in the cold.
Mercurous nitrate	Very dense, grayish-black precipitate.
Nickel hydroxide in water	Unchanged.
Ferric hydroxide in water	Unchanged.
Ferric chloride	Decided but incomplete reduction to ferrous chloride.
Yellow oxide of mercury in water	Unchanged.
Osmic acid	Rapidly reduced.
Potassium rutheniate	Very slowly and incompletely reduced.
Cuprous chloride	White crystalline precipitate, soluble in hydrochloric acid and reprecipitated by ammonia. Turns brown on washing with water.
Cupric chloride	Unchanged.
Iridium chloride	Yellow precipitate, resembling the platinum compound.
Hydrogen peroxide	No oxidation to sulphuric acid occurs.
Potassium ferricyanide	Very slow reduction to ferrocyanide.
Potassium bichromate acidulated with hydrochloric acid.	Very slight reduction. No sulphuric acid is formed.
Cerium dioxide dissolved in sulphuric acid.	Quickly bleached.

Precipitated carbonate of copper....	These substances, tried separately in water, remained unchanged.
Litharge.....	
White lead.....	
Lead chromate.....	
Silver foil in water.....	Unchanged.

Comments.—The metallic compounds of methyl sulphide are, without exception, more soluble than those of methyl hydrosulphide. No insoluble compounds of methyl sulphide have yet been found. Towards oxidizing agents, methyl sulphide is as stable as methyl hydrosulphide. In no case was a trace of sulphuric acid produced, although the gas was subjected to the action of many very powerful oxidizing agents. The gold-chloride reaction is similar to that produced by methyl hydrosulphide.

Carbon oxysulphide is sharply distinguished from methyl sulphide and hydrosulphide by the ease with which it is oxidized to sulphuric acid by many oxidizing agents, such as bromine-water or potassium permanganate in acid solution; moreover, the separation of sulphuretted hydrogen from carbon oxysulphide is easily effected, as already stated, by the yellow oxide of mercury.

Although not altogether satisfactory, the following plan may be used to recognize small quantities of methyl sulphide: The gas is passed through a small quantity of weak palladium-chloride solution heated nearly to 100°. On spontaneous evaporation, the solution deposits monoclinic crystals easily recognized under the microscope. If the mercaptan compound appears (cinnamon-colored powder) the solution may be boiled. The methyl-sulphide compound then goes into solution. The mercaptan compound is insoluble. On evaporating the filtrate, the methyl-sulphide compound crystallizes in monoclinic prisms. If sulphuretted hydrogen and methyl hydrosulphide are suspected to occur, these two gases may be completely absorbed by caustic soda. The methyl sulphide is unabsorbed by soda, and by warming the soda solution it may be prevented from condensing upon the surface of the liquid. By using a solution of lead oxide in caustic soda, which absorbs sulphuretted hydrogen and methyl hydrosulphide, it is possible afterwards to expel the methyl hydrosulphide by cautious addition of dilute hydrochloric acid, the sulphuretted hydrogen being then held back by the lead as

lead sulphide.[1] Lastly, the terrible odor of the methyl hydrosulphide is sufficient for its identification under all circumstances.

Nitrogen.

Although readily prepared by the absorption of oxygen from air by pyrogallol, the resulting nitrogen contains carbon monoxide, as shown by Tacke.[2] Ferrous sulphate in an excess of alkaline citrate-solution is unsatisfactory as an absorbent for atmospheric oxygen on account of the extreme slowness of its action. I have found that ferrous chloride mixed with thick milk of lime acts more rapidly for the reason that, on agitating in a glass vessel, the pasty mass coats the walls and better exposure of the precipitated ferrous hydrate to the air is effected. The nitrogen used in the following experiments was prepared as described below.

Air was shaken with a mixture of pyrogallol and caustic soda solution. The resulting impure nitrogen was caused to pass slowly through a heated combustion-tube filled partly with metallic copper (reduced by hydrogen from copper oxide) and partly with copper oxide.

Leduc[3] has shown that copper used to remove oxygen from air should be made by the reduction of copper oxide at a low temperature, in order to avoid the formation of copper hydride and consequent contamination of the nitrogen by hydrogen. This impurity may, however, be removed by using some copper oxide in the heated tube. It may be stated that in a series of experiments, using pyrogallol and alkali in different proportions and in different degrees of concentration, it was not possible to obtain pure nitrogen. In every case the gas was found to exert a slight reducing action upon palladium-chloride solution. The compounds of nitrogen result usually by indirect processes from other compounds. Additive reactions are rare.

Merz[4] has shown that magnesium heated to redness in nitrogen produces a nitride. The nitride so formed is stable in dry air, but yields magnesium hydrate and ammonia in presence of moisture. So great is the affinity of magnesium for nitrogen that, on burning in moist air, the same compound results. The oxide formed always contains ammonia as a decomposition-product of this

[1] Klason: *loc. cit.*
[2] Arch. f. d. ges. Physiol. **38**, 401 (1886); Ber. d. chem. Ges. **19**, Ref. 793.
[3] Compt. Rend. **113**, 71.
[4] Ber. d. chem. Ges. **24**, 3940 (1891).

nitride.[1] The combination of nitrogen and magnesium could only prove of interest as a gas-reaction in case the formation of the compound is not interfered with by the presence of such gases as are not readily removable from a mixture. Sulphur and oxygen compounds would naturally be decomposed by magnesium.

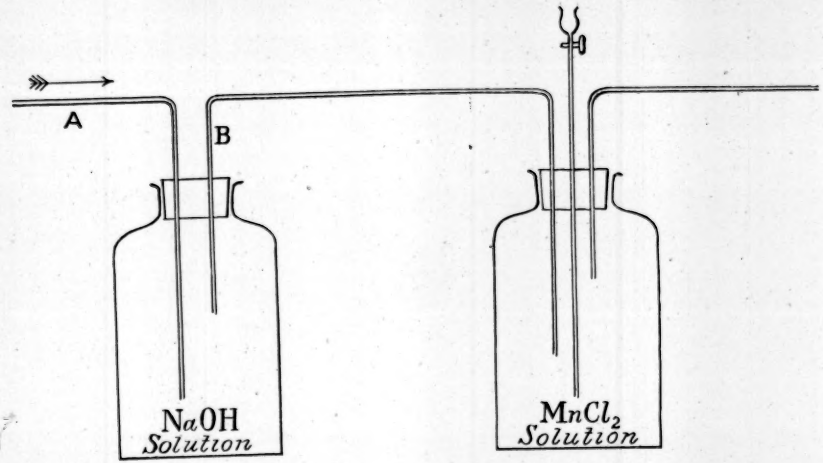
In experiments with natural gas, as supplied to Allegheny in October, 1892, it was found that magnesium heated to redness in a stream of the gas for one-half hour yielded a strong odor and the usual reactions characteristic of ammonia on moistening. The compound produced exhaled ammonia on exposure to air. Nitrogen also unites directly with lithium and potassium. Ouvrard[2] obtained a nitride of lithium containing 50.28 per cent. of nitrogen.

Oxygen—Reactions.

The presence of oxygen in very small quantities in a gas-mixture is easily recognized by the change of color produced in a precipitate of ferrous ferrocyanide or manganous hydroxide, or in a solution of pyrogallol in soda, or indigo solution previously bleached by zinc dust. All of these substances absorb oxygen and at the same time undergo a change of color. The most sensitive of these is the mixture of pyrogallol and alkali. A very sensitive reagent for free oxygen is found in precipitated manganous hydroxide in water, which, by reason of very complete oxygen absorption, changes into manganic hydroxide, Mn_2O_3, its color changing at the same time from white to brown. The following process is a modification of Winkler's method[3] for the determination of dissolved oxygen in water.

Two bottles of about two ounces capacity are connected as shown in the sketch. The gas stream enters by *A* and bubbles through soda solution and manganous chloride consecutively. After complete expulsion of air by the gas current, the tube *B* is pushed down so that some of the soda solution is forced over into the manganous-chloride solution, causing a precipitation of manganous hydroxide. This precipitate remains white in the absence of oxygen. If oxygen be present, it gradually darkens in changing to manganic hydroxide. On adding now a little iodide of potassium solution and then sulphuric acid, by the tap-funnel,

[1] Aslanoglou: Chem. News **62**, 99 (1890).
[2] Compt. Rend. **112**, 120 (1891); Ber. d. chem. Ges. **25**, Ref. 104.
[3] Ber. d. chem. Ges. **22**, 1764 (1889); Ztschr. ang. Chem. 1891, p. 105.


A
B
NaOH
Solution
MnCl2
Solution

the oxide of manganese redissolves, liberating iodine, recognizable by its color even when the most minute traces only of oxygen are present. The same apparatus can be used for pyrogallol and soda.

The method above described is very satisfactory in testing for oxygen in presence of paraffins, olefines, acetylene, allylene, carbon monoxide, or carbon-disulphide vapor. Sulphuretted hydrogen and carbon oxysulphide must be absorbed by ammoniacal cadmium-chloride solution, or other suitable reagent, before the test can be applied. If an ammoniacal cadmium-chloride solution is thus used, vapors of ammonia must be absorbed by dilute sulphuric acid before the reaction is tried. No difficulty occurs in applying the same reaction in testing a limited volume of gas. Instead of conducting the gas in a stream through the solutions, a eudiometer may be used. The reaction is, however, far less satisfactory, as the solutions are liable to hold atmospheric oxygen dissolved. By means of a standard hyposulphite-solution the free iodine may be estimated; and, as 254 parts of iodine correspond to 16 parts of oxygen, the latter element is easily determined.

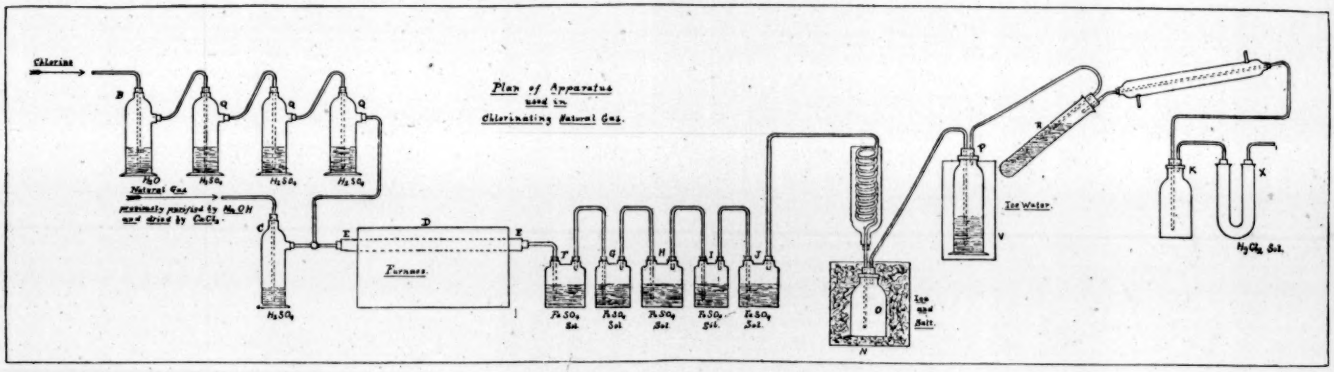
Von der Pfordten[1] proposes the use of chromous chloride in presence of sodium acetate for the quantitative determination (by absorption) of oxygen in a gas-mixture. According to this author, the change from colorless to greenish blue renders the solution a suitable reagent for the recognition of oxygen. Very minute quantities of oxygen can be detected. The preparation of the reagent (reduction from chromic chloride by zinc in presence of hydrochloric acid) is effected in a Woulfe bottle, through which the gas is already passing, and the air is thus removed previous to the test.

Fuming sulphuric acid is said to dissolve oxygen.[2]

Nothing need be said here concerning the detection of oxygen when occurring in large quantities in a gas-mixture.

The general study of gas reactions has not yet attracted the attention it deserves. The majority of articles bearing upon the subject have referred only incidentally to reactions by which a particular gas, or group of gases, may be recognized. Every effort has been made to cite references to all published statements

[1] Ztschr. anal. Chem. **26**, 74 (1887).
[2] Lean and Bone: J. Chem. Soc. **61**, 879 (1892).


Chlorine
B
Q
Q
Q
H_2O
H_2SO_4
H_2SO_4
H_2SO_4
Natural Gas
previously purified by NaOH
and dried by $CaCl_2$.
C
H_2SO_4
E
D
Furnace.
F
F
F
G
H
I
J
K_2SO_4 Sat.
K_2SO_4 Sol.
K_2SO_4 Sat.
K_2SO_4 Sol.
K_2SO_4 Sol.
Plan of Apparatus
used in
Chlorinating Natural Gas.
O
Ice and Salt.
N
P
V
R
Ice Water.
K
X
$HgCl_2$ Sol.

concerning reactions which I have detailed. It is probable, however, that many have been overlooked. In conclusion, I have to express my thanks to Messrs. R. B. Carnahan, Gustav Miller and Henry Phillips, for assistance in the work, and especially to Mr. Henry T. Weed.

III.—Substitution-products of the Action of Chlorine upon Methane.

Natural gas was used in the following experiment. The gas was collected in June, 1888, from main conveying gas directly from Murraysville to Pittsburgh. A steel cylinder provided with thoroughly tested valves was filled from the gas main under a pressure of eighty pounds. An analysis of the gas showed it to have the following composition:

Methane	95.40
Carbon dioxide	0.20
Carbon monoxide	0.
Ethylene	0.
Hydrogen	0.
Oxygen	trace.
Nitrogen	4 40
	100.00

The following is an outline of the process of treatment:

Chlorine was generated in a large flask and washed in *B* before drying in *Q*. Natural gas was freed from carbon dioxide by caustic soda, and then dried by sulphuric acid. *Q* and *C* served at the same time to regulate the flow. *E* is a glass combustion-tube which was filled with bone-black previously washed by hydrochloric acid. It was sought to produce the reaction:

$$CH_4 + 2Cl = CH_3Cl + HCl.$$

The furnace *D* was kept at the lowest possible temperature necessary to cause the color of the chlorine to disappear. After passing this tube, the gases were conducted through several bottles of ferrous-chloride solution to remove any excess of chlorine, as well as hydrochloric acid. A reaction occurred at once in *E:* the chlorine disappeared. Too high a temperature caused a pale flame to appear in the combustion-tube, which invariably led

to a deposit of carbon. It was found necessary to maintain a very low temperature in the combustion-tube. Slight condensation of a clear liquid occurred in *O*. Whether an excess of chlorine, or an insufficient quantity, or the theoretical quantity for the above reaction was used, there was formed continuously the tetrachloride of carbon, which collected in oily drops in *F* and *G*.

From experiments in using different proportions of chlorine and methane, employing higher and lower temperatures, and when sand or asbestos was substituted for the bone-black, and in using an empty combustion-tube, I am led to the conclusion that the tendency is always to form methyl chloride and carbon tetrachloride; but that the intermediate products, dichlormethane CH_2Cl_2, and chloroform $CHCl_3$, are formed only in relatively small quantity.

The manufacture of chloroform from natural gas, so far as these experiments indicate, is likely to prove a matter of difficulty. The gas escaping from *O* has the odor of methyl chloride from methyl alcohol, is readily soluble in water and in alcohol, and burns with a green flame. The gas, after leaving *P*, passed into a solution of potassium hydrosulphide in *R* and then on into a solution of mercuric chloride in *X*. An immediate and copious precipitation occurred in *X*.

Methyl chloride from methyl alcohol, as is well known, is characterized by the property of forming a solid crystalline hydrate when conducted into ice-water. The gas, prepared by the method above described, was passed through the bottle *P* containing broken ice while the ice was slowly melting, but no trace of a crystalline hydrate appeared.

It was not attempted to analyze the gas, for the reason that an analysis of a mixture of methyl chloride with some unaltered methane and traces of the higher chlorides would lead to very uncertain results. The odor, the solubility in alcohol, the green color of the flame and the reaction with potassium hydrosulphide, all tend to show that it was methyl chloride. The failure to produce the crystalline hydrate with ice-water I cannot explain.

It has long been considered a settled fact that only one methyl chloride is possible, Berthelot having shown[1] that when methyl chloride from methane and chlorine is treated with potash, saponification results with production of methyl alcohol, just as in the

[1] Compt. Rend. **43**, 916.

case of methyl chloride from wood-spirit and hydrochloric acid. Von Baeyer[1] states that methyl chloride prepared from methyl alcohol and hydrochloric acid is different from the methyl chloride obtained by the action of chlorine on methane in the fact that the chloride from the latter source fails to form a crystalline hydrate when led into ice-water, and that there are, therefore, two compounds isomeric, but not identical, having the formula CH_3Cl.

Roscoe and Schorlemmer[2] explain the failure to form a crystalline hydrate by the methyl chloride from methane, on the ground that other chlorinated substitution-products occur with the methyl chloride. My experiments lead me to think that this does not satisfactorily explain the difference. Dichlormethane and chloroform do not occur except in traces in the gas which was produced, while carbon tetrachloride was easily condensed in *F* and *G*, as it boils at 78°. It cannot therefore contaminate the methyl chloride.

The methyl chloride formed in the apparatus above described was caused to pass through a second combustion-tube heated in a furnace, and through a side tube a stream of chlorine was passed directly into this second combustion-tube. The methyl chloride supposed to have been formed by the action in the first furnace received, therefore, an additional quantity of chlorine before passing through the combustion-tube in the second furnace. It seemed possible that in such a case the formation of higher chlorinated derivatives might thus be better controlled. The equation $CH_4 + 2Cl = CH_3Cl + HCl$ probably represents the reaction occurring in the first combustion-tube. The gases were then passed through water to remove hydrochloric acid. They were then dried by sulphuric acid and received the additional volume of chlorine, as above mentioned, before entering the second heated combustion-tube. This reaction might then occur:

$$CH_3Cl + 2Cl = CH_2Cl_2 + HCl.$$

In the second tube the results were hardly different from those originally obtained. The methane tends constantly to produce methyl chloride or carbon tetrachloride, and there is little or no probability of obtaining intermediate products except in relatively very small proportions.

[1] Ann. Chem. (Liebig) **107**, 269 (1858); see also Watt's Dic. (1st Ed.), Vol. III, p. 987.
[2] Vol. III, Pt. 1, p. 203.

IV.—Preparation of Halogen Compounds of Alkyls and Olefines.

The alkyl iodides serve as the most convenient source for the preparation of the paraffins by the Gladstone and Tribe reaction, to which reference has already been frequently made, *e. g.*:

$$CH_3I + Zn + H_2O = Zn\langle^{I}_{OH} + CH_4.$$

The same compounds find application in forming the olefines by the action of potash in alcoholic solution. Thus:

$$C_3H_7I + KOH = C_3H_6 + KI + H_2O.$$

The olefine dibromides are of service in the preparation of olefines by means of zinc which abstracts the halogen, liberating the olefine. The acetylenes are most conveniently produced from the olefine dibromides, by the action of alcoholic potash, according to the reaction:

$$C_3H_6Br_2 + 2KOH = C_3H_2 + 2KBr + 2H_2O.$$

Hence, the selection of convenient methods in forming these iodine and bromine compounds has become a matter of much importance in the study of gas-reactions.

The alkyl iodides are most easily formed by the action of iodine upon a mixture of red phosphorus and alcohol. Chancel[1] has given a very convenient method for the preparation of propyl iodide and similar compounds. 127 grams iodine, 60 grams propyl alcohol and 10 grams of red phosphorus are mixed in a flask, and, after the reaction, which at once sets in, has subsided, the flask is to be heated for an hour, connected with a reversed condenser. After cooling, the oily liquid is decanted, washed with soda solution and dried by calcium chloride. On distilling, nearly 90 per cent. of the theoretical yield is obtained. This method gives very satisfactory results, and is applicable in the case of methyl iodide, ethyl iodide, propyl iodide, etc.

The process commonly recommended for the preparation of ethyl bromide by the addition of bromine to a mixture of ethyl alcohol and red phosphorus, yields a small and impure product, and is difficult to control. Erlenmeyer[2] has given an excellent method for the preparation of ethyl bromide by the distillation of

[1] Bull. Soc. chim. (Paris) [2] **39**, 648 (1883); Ber. d. chem. Ges. **16**, 2286.
[2] Jsb. 1878, 538.

a mixture of potassium bromide, sulphuric acid and alcohol. Both of these processes yield a product largely contaminated by ether which, although not removable by fractionation, may be completely separated from the ethyl bromide by digestion with sulphuric acid in the cold.[1]

The olefine dibromides can be most easily prepared by the direct union of olefine with bromine. Meyer[2] has, however, shown that in presence of iron (wire) as an "Ueberträger," bromine attack ethyl bromide, producing the reaction:

$$C_2H_5Br + 2Br = C_2H_4Br_2 + HBr.$$

This process, which requires heating in sealed tubes, in the case of ethyl bromide yields propylene dibromide in the cold from propyl bromide. The method is open to the objection that large volumes of hydrobromic acid gas are necessarily evolved. Moisture wholly arrests the reaction. Experiments tried in this laboratory with other metals (palladium, magnesium, aluminium) as "Bromüberträger" and at varying temperatures, have failed to give satisfactory results in preparing ethylene dibromide. Not only heat, but pressure in sealed tubes is also necessary.

Allyl iodide, which has served as a more convenient material for the preparation of propylene than propyl iodide, was made by the action of iodine upon glycerine in the presence of both red and yellow phosphorus, by the excellent method described by Behal.[3]

Iodides are to be preferred to bromides in all cases where potash is used to produce a reaction, as potassium iodide is more soluble in alcohol than potassium bromide. For this reason a larger quantity of potash is necessary for a given reaction (formation of olefine from alkyl bromide) than in case of the iodine compound.

[*To be continued.*]

[1] *Vide* Riedel; Ber. d. chem. Ges. **24**, Ref. 105.
[2] Ber. d. chem. Ges. **24**, 4248 (1891).
[3] Bull. Soc. chim. (Paris) [2] **47**, 875 (1887); Ber. d. chem. Ges. **20**, Ref. 693.

Contribution from the Chemical Laboratory of Purdue University.

XI.—A REDUCTION-PRODUCT OF ORTHOSULPHOBENZOIC CHLORIDE.

By Walter Jones.

The action of sodium hydrosulphide on phthalyl chloride has been studied by Graebe and Zschokke,[1] who obtained among other products the thio-anhydride of phthalic acid. The conduct of this compound leaves little doubt concerning its constitution, for by treatment with resorcin under different conditions either an oxygen or a sulphur atom may be replaced by resorcin residues. It is therefore concluded that the structure of the compound is represented by the unsymmetrical formula $C_6H_4<\begin{matrix}CS\\CO\end{matrix}>O$.

With the expectation of obtaining a similar compound, the chloride of orthosulphobenzoic acid was treated with potassium hydrosulphide. In this case, however, potassium hydrosulphide acts as a reducing agent: sulphur is thrown down, sulphuretted hydrogen evolved, and a compound is formed whose analysis corresponds to the formula for sulphonphthalide, $C_6H_4<\begin{matrix}CH_2\\SO_2\end{matrix}>O$.

The chloride which was used for this purpose was prepared by treating the acid ammonium salt of orthosulphobenzoic acid with phosphorus pentachloride.[2] 10 grams of the oil thus obtained were added, a drop at a time, to a solution of potassium hydrosulphide which represents 10 grams of caustic potash in 150 cc. of water. At ordinary temperatures the substances do not react, but on warming sulphur begins to separate, the oil passes into solution, and at the same time there is an evolution of sulphuretted hydrogen. As the action proceeds heat is produced sufficient to boil the liquid and thus cause undesirable results. The vessel containing the materials should therefore be placed in cold water after the reaction has started, and should be shaken continually in order to prevent inclusion of the oil by the separated sulphur. At the end the materials are warmed on a water-bath. The liquid is now filtered through an asbestos filter on the top of which has been placed some flowers of sulphur. This process removes nearly all of the sulphur. The yellow filtrate is diluted with

[1] Ber. d. chem. Ges. **17**, 1175. [2] This Journal **11**, 332.

about 2 liters of water, heated to boiling and acidified with hydrochloric acid. A copious precipitate is produced which consists of sulphur and the compound sought; the greater part of the latter, however, remains in solution and separates as a poorly crystalline mass when the filtered solution cools. A further yield may be obtained if the material on the filter is warmed with potassium hydrosulphide and the process repeated. The compound which is precipitated from hot water will not dissolve on heating with the same solution from which it was precipitated. If, however, sulphuretted hydrogen is passed in, the compound dissolves and is again precipitated on cooling. The product was crystallized from alcohol and analyzed, with the following results:

I. 0.2234 gram gave 0.4057 gram CO_2 and 0.0709 gram H_2O.

II. 0.2419 gram gave 0.4382 gram CO_2 and 0.0780 gram H_2O.

III. 0.2193 gram gave 0.3009 gram $BaSO_4$.

IV. 0.1994 gram gave 0.2740 gram $BaSO_4$.

	Theoretical for $C_7H_4SO_3$.	Found. I.	II.	III.	IV.
C	49.38	49.52	49.40	...	...
H	3.54	3.52	3.59	...	...
S	18.85	...	...	18.85	18.88

The formation of a compound of this composition under the conditions stated would suggest the treatment of the chloride with simple reducing agents. The action of nascent hydrogen was studied and the compound obtained was found to be identical with that formed by the use of potassium hydrosulphide.

5 grams of the chloride were dissolved in ether and placed in an Erlenmeyer flask which had been filled nearly to the top with granulated zinc. The flask is placed in ice-cold water and a few drops of dilute hydrochloric acid added from time to time during 12–16 hours. The products of the reaction are allowed to stand in a cool place for 24 hours. As the ether evaporates the product deposits on the zinc. The acid solution is poured off and dilute alkali placed in the vessel. The organic compound dissolves and, after filtering from the zinc, is precipitated by acid. Dissolving in an alkali, filtering and precipitating with an acid, is repeated several times to remove traces of zinc chloride, and the compound is finally crystallized from alcohol.

I. 0.1872 gram gave 0.3401 gram CO_2 and 0.0595 gram H_2O.

II. 0.2003 gram gave 0.3619 gram CO_2 and 0.0638 gram H_2O.

III. 0.3013 gram gave 0.4150 gram $BaSO_4$.
IV. 0.2885 gram gave 0.3960 gram $BaSO_4$.

	Theoretical for $C_7H_4SO_3$.	Found. I.	II.	III.	IV.
C	49.38	49.54	49.22	...	...
H	3.54	3.53	3.54	...	...
S	18.85	...	...	18.92	18.86

The two substances prepared by these two methods of reduction are identical in all their chemical and physical properties. The compound melts and decomposes at 287°–289°. It is insoluble in water, soluble in alcohol and in ether. The crystals obtained from alcohol are difficult to dissolve again; but if dissolved in ammonia or alkali and precipitated by an acid, the material can easily be dissolved in alcohol. It reduces permanganate solution, and is oxidized to orthosulphobenzoic acid by the action of boiling concentrated nitric acid. The substance obtained by dissolving the crystalline compound in alkali and precipitating with an acid can be oxidized almost instantaneously by warming with dilute nitric acid. When this precipitated material has been dried it requires concentrated acid and continued heating for its oxidation. When warmed with resorcin and concentrated sulphuric acid a compound is formed whose alkaline solution shows a fine eosin fluorescence. This reaction suggests the thio-anhydride, but as the body which is formed in the reaction with zinc and hydrochloric acid also produces a fluorescent compound, and as the fluorescent compound cannot be produced without the assistance of sulphuric acid, the conclusion follows that oxidation takes place before a phthaleïn is formed.

All attempts to unite the compound with ammonia or alkaline sulphites failed to produce crystalline bodies. An attempt was made to prepare an ammonium salt by allowing a slightly alkaline solution in ammonia slowly to evaporate; ammonia gradually escaped and the original compound was deposited. By boiling a solution in ammonia with barium carbonate, ammonia is driven out, but as the filtered solution is slowly evaporated, barium hydroxide crystallizes and the original substance is deposited.

It has been shown[1] that the chloride of orthosulphobenzoic acid made by treating the acid ammonium salt with phosphorus pentachloride consists of two substances, one of which separates

[1] Ber. d. chem. Ges. **26**, 2634.

in fine crystalline form when the mixture is allowed to stand at the ordinary temperature; and that the difference between these two isomeric chlorides is probably expressed by formulæ similar to those which have in turn been offered for phthalyl chloride. It was at first supposed that the compound which is the subject of this paper is a mixture of two isomeric substances resulting from the two isomeric chlorides. This explanation of several apparent anomalies noted above is insufficient, for it was found that the crystalline chloride which separates from the oil on standing, produces with potassium hydrosulphide a compound which is soluble in water and dilute acids. Moreover, there is in this case no separation of sulphur. This reaction is now under investigation.

It would seem that a compound whose composition is expressed by the formula $C_7H_6SO_3$, formed by the reduction of one of the chlorides of orthosulphobenzoic acid, must be represented structurally by one of the two formulæ:

$$\text{I. } C_6H_4\begin{cases}CH_2\\SO_2\end{cases}O \qquad \text{II. } C_6H_4\begin{cases}COH\\SO.OH\end{cases}.$$

The properties of the compound which have been mentioned suggest that it is not an aldehyde; that it is not easily reduced; that it forms soluble salts with alkalies, which yield an acid first, then an anhydride when their solutions are acidified with a mineral acid; that the compound yields with sulphuretted hydrogen a thio-acid which is soluble in hot water, but as the solution cools sulphuretted hydrogen is eliminated and an anhydride is formed. While these indications do not by any means constitute a proof, they may nevertheless be considered as evidence, since they all point to the same formula.

March, 1894.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON NITROGEN HALOGEN COMPOUNDS.

THIRD PAPER.

BY FELIX LENGFELD AND JULIUS STIEGLITZ.

Notwithstanding our two previous papers[1] on the replacement of the halogen in halogen amides by organic radicles, in which we state that we are endeavoring by the use of compounds with more positive and more negative radicles attached to the group -CONH "Hal"- to effect the substitution without the rearrangement observed, C. E. Linebarger has just published in this Journal[2] an article on the replacement of the halogen in benzoyl halogen amides by other radicles, the results of which, by the way, were purely negative. It is evident that Mr. Linebarger has not read our papers, as it is obvious that benzbromamide must be one of the first substances investigated. In fact, one of our students, Mr. O. K. Folin, is now studying the reactions of benzbromamide in the direction indicated in our former articles. The following observations were made by us some time ago:

Action of Sodium Methylate on Paranitrobenzbromamide.—1 gram sodium was dissolved in 100 grams methyl alcohol, and 11 grams paranitrobenzbromamide was added, after which the solution was boiled for one hour and filtered while hot. On cooling, light-yellow crystals, melting at 176°, were deposited. The filtrate was further concentrated and two other crops of crystals obtained, which on solution in chloroform and precipitation with ligroïn, melted at 176°. The residue, after complete evaporation of the chloroform, consisted of a yellow mass melting at 120°–125°, and on recrystallization from chloroform, at 126°–128°. It was found to be a mixture of the substance melting at 176° and paranitraniline. On leading hydrochloric acid into its chloroform solution a flaky, crystalline, very slightly colored (pink) substance, melting at 200°–205° with decomposition, was precipitated. It is probably the chloride of paranitraniline, from which it may readily be obtained. Thrown into water it gives a yellow precipitate melting at 148° and having all the characteristics of paranitraniline. From chloroform solution ligroïn precipitates light-yellow crystals melt-

[1] This Journal **15**, 215, 504. [2] *Ibid.* **16**, 216.

ing at 176°, and identical with those described above. The various fractions melting at 176° were united, recrystallized from acetone and analyzed.

0.2219 gram gave 28.7 cc. moist nitrogen at 18° and 747 mm.

Calculated for $C_8H_8N_2O_4$.	Found.
14.28	14.57

To determine if there had been rearrangement in the replacement of bromine by the methoxy group, the methyl ester of paranitrophenylcarbamic acid was prepared and found to be identical with the substance melting at 176°. Therefore the main product of the action of sodium methylate in methyl-alcohol solution on paranitrobenzbromamide is methyl paranitrophenylcarbamate, which on decomposition yields paranitraniline.

Methyl Paranitrophenylcarbamate, $NO_2.C_6H_4.NH.COOCH_3(p)$. —7.5 grams paranitraniline was dissolved in 100 grams chloroform, 2.5 grams methyl chlorformate added, the whole boiled for two hours and filtered. On evaporation the chloroform left a yellow residue which contained no chlorine and melted at 128°. The melting-point remained constant even after repeated recrystallization and precipitation by ligroïn from chloroform solution, but analysis indicated that it was a mixture of paranitraniline and methyl paranitrophenylcarbamate. It was therefore dissolved in chloroform and hydrochloric acid led in. Paranitraniline chloride was precipitated, and on now adding ligroïn to the chloroform solution, very light yellow crystals melting at 176° were obtained. The same result is obtained by repeatedly washing with boiling water the substance melting at 128°. The residue melts at 176° on recrystallization from acetone. Analysis gave the following: 0.1222 gram substance gave 15.2 cc. moist nitrogen at 12.5° and 736 mm.

Calculated for $NO_2.C_6H_4.NH.CO_2CH_3$.	Found.
14.28	14.30

Methyl paranitrophenylcarbamate is a light-yellow, almost colorless crystalline substance, insoluble in ligroïn and water; slightly soluble in ether or benzene; soluble in chloroform, acetone and alcohol. Carefully heated, it volatilizes without decomposition; rapidly heated, it explodes. It melts at 176°, softening, when heated slowly, at 172°–173°.

Action of Sodium Methylate on Acetobromamide: Methyl Methylcarbamate, $CH_3NHCOOCH_3$.—4 grams sodium was dissolved in 250 grams methyl alcohol, 24 grams acetobromamide added and the liquid boiled for two hours. As it was still alkaline, a few drops of hydrochloric acid were added, the neutral solution evaporated, and the residue extracted with chloroform in a Soxhlet's apparatus. The chloroform solution was washed with water, dried with calcium chloride and evaporated in the water-bath. The residue, a colorless oil, distilled at 55°–60° under a pressure of 25 mm., and at 158° at ordinary pressure. It has a peculiar, not unpleasant, odor; is soluble in water, alcohol, chloroform and benzene, and insoluble in ligroïn. Analysis gave the following:

0.119 gram substance gave 16.5 cc. moist nitrogen at 22° at 748 mm.

Calculated for $C_3H_7NO_2$.	Found.
15.6	15.2

As the analysis, boiling-point, etc., agreed with the properties of the methyl ester of the methylcarbamic acid first prepared by Franchimont and Klobbie,[1] some of the ester was prepared by their method. The two were found to be absolutely identical.

CHICAGO, *March*, 1894.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON THE ADDITION-PRODUCTS OF THE AROMATIC ISOCYANIDES.

BY WARREN K. SMITH.

The compounds known as isocyanides were discovered almost simultaneously by Hofmann[2] and by Gautier.[3] The latter supposed them to be bases, $\left.\begin{matrix}R\\C^{II}\end{matrix}\right\}N^{III}$, reacting with haloid acids like ammonia, giving $\left.\begin{matrix}R\\C^{II}\end{matrix}\right\}N^{V}.HX$. For this reason he called them carbylamines. That the isocyanides have no basic properties

[1] Recueil trav. chim. **7**, 343; Ber. d. chem. Ges. **23**, Ref. 296.
[2] Ann. Chem. (Liebig) **144**, 114; **146**, 107. [3] Ann. chim. phys. [4] **17**, 103.

was shown by Nef,[1] who studied exhaustively the phenyl and *o*-tolyl isocyanides. Nef was the first to grasp the fact that the most characteristic property of the isonitriles is their power of adding to the carbon atom of the isocyanogen radicle, two monovalent atoms or groups, thus proving the presence of bivalent carbon.

The work which follows was carried out under the direction of Dr. Nef and consists chiefly of a general study of the addition-products of *p*-tolyl isocyanide and a study of some of the reactions of one of the addition-products of phenyl isocyanide.

As is to be expected, the reactivity of *p*-tolyl isocyanide is about the same as that of the other aromatic isonitriles and its addition-products are similar. Besides the addition of chlorine, which was accomplished by Nef,[2] the author has effected the following additions:

1. Of sulphur; forming *p*-tolyl mustard-oil:

$$C_7H_7N:C + S = C_7H_7N:C:S.$$

2. Of sulphuretted hydrogen, and mercaptans; giving thioform-*p*-toluide and its alkyl ethers:

$$C_7H_7N:C + H_2S = C_7H_7N:C{<}^{H}_{SH},$$

$$C_7H_7N:C + RSH = C_7H_7N:C{<}^{H}_{SR}.$$

3. Of alcohols; giving imidoformic ethers:

$$C_7H_7N:C + ROH = C_7H_7N:C{<}^{H}_{OR}.$$

4. Of hydrogen; giving methyl-*p*-toluidine:

$$C_7H_7N:C + 4H = C_7H_7NHCH_3.$$

5. Of amines, giving amidines:

$$C_7H_7N:C + RNH_2 = C_7H_7N:C{<}^{H}_{NHR}.$$

6. Of organic-acid chlorides, giving imide chlorides:

$$C_7H_7N:C + R.COCl = C_7H_7N:C{<}^{Cl}_{CO.R}.$$

Preparation of Paratolyl Isocyanide.[3]

This substance was made according to Hofmann's method for the preparation of the isonitriles. The yield is always poor, the

[1] Ann. Chem. (Liebig) **270**, 267. [2] *Ibid.* **270**, 321.
[3] Nef: Ann. Chem. (Liebig) **270**, 320.

best being obtained as follows: A solution of 210 grams caustic potash in 800 cc. alcohol (95 per cent.) is warmed to about 50° and a solution of 100 grams *p*-toluidine in 190 grams chloroform is slowly added by means of a dropping-funnel. Reaction at once sets in, accompanied by the separation of potassium chloride and the evolution of heat. It is necessary to cool continually, the temperature being best kept at a little over 50°. The reaction is much less violent toward the end and is never complete. After standing a short time, the alcohol and unchanged chloroform are distilled off on the water-bath, and the residue, after the addition of a quantity of water sufficient to dissolve the potassium chloride, is distilled with steam. A mixture of *p*-toluidine and *p*-tolyl isocyanide goes over as an oil of slight yellow color. This is taken up with ether and washed with 120 grams hydrochloric acid (sp. gr. 1.20), previously divided into two portions and largely diluted. It is best to do this washing as rapidly as possible, for the isocyanides react very easily with the amine hydrochlorides.[1] To this end it is well to dilute the hydrochloric acid as much as the size of the separatory funnel used will allow, and to warm it to about 30°; for otherwise the di-*p*-tolylformamidine, which is always formed, gives troublesome emulsions, as it is only slightly soluble in cold water. As soon as the amidine hydrochloride is all removed by washing with water the ethereal solution is washed once with dilute alkali and dried over caustic potash. After distilling off the ether, the isonitrile is distilled at reduced pressure.

Paratolyl isocyanide boils at 99°[2] at 32 mm. pressure ("99° at 36 mm." [Nef]), and has a specific gravity of 0.96 at 24° (Westphal). On cooling it solidifies to a crystalline solid which melts at 21°. Its odor does not differ much from that of the other aromatic isonitriles, being less disagreeable than that of phenyl isocyanide. Its taste is extremely bitter, as may be noticed by inhaling a small quantity of its vapor at ordinary temperatures. No unpleasant physiological effects were experienced by the author in working with this substance. When first distilled it is colorless, but immediately begins to take on a green color and finally becomes brown. It is best kept in the dark at

[1] See p. 380.

[2] The temperatures given in this paper were measured by a thermometer which was carefully compared with a standard set of Gerhardt's short thermometers. At no point between 0 and 200° was there a variation of one degree.

a temperature below its melting-point. Under these conditions it may be kept for several weeks with only slight change. On heating polymerization takes place, interfering with such reactions of this compound as require a high temperature for their accomplishment.

Action of Sulphur.—5 grams *p*-tolyl isocyanide and the calculated amount of sulphur dissolved in carbon disulphide were heated in a sealed tube for six hours at 120°–140°. On opening the tube no smell of isocyanide was left. After the carbon disulphide had been distilled off, the mustard-oil was separated from the polymerized isonitrile by distilling with steam. The distillate was extracted with ether and the solution dried with chloride of calcium. After distilling off the ether the mustard-oil boiled at 242°–243° and melted at 26°. Hofmann[1] gives the boiling-point 237° and the melting-point 26°. Sulphur was determined by the method of Carius.

0.1538 gram substance gave 0.2409 gram $BaSO_4$.

	Calculated for C_8H_7NS.	Found.
S	21.47	21.55

Paratolyl isocyanide seems to have a great tendency to take up sulphur from the compounds of sulphur with the halogens and form mustard-oils. A solution of bromine in carbon bisulphide when treated with isocyanide gave considerable quantities of mustard-oil. The odor of mustard-oil was noticed on vulcanized rubber which had been exposed for some time to the vapor of isonitrile. Mustard-oil was the only compound that could be isolated from the substances obtained by the reaction of thiophosgene on isocyanide.

Sulphur monochloride and *p*-tolyl isocyanide react with great violence. Several experiments were carried out, using carbon disulphide as a diluent. Five grams isocyanide and 3 grams sulphur monochloride were used in each experiment. The only products that could be identified were polymerized isonitrile and mustard-oil, the latter being obtained in quantities varying from 2.5 to 4 grams in the several experiments.

5 grams *p*-tolyl isocyanide and 2.2 grams sulphur dichloride were mixed in carbon-disulphide solution, moisture was carefully excluded, and the mixture was cooled by means of salt and ice.

[1] Ber. d. chem. Ges. **1**, 173.

On boiling off the carbon disulphide and distilling with steam, 3.5 grams of an oil were obtained which, after taking up with ether and drying, boiled from 225°–240°. This was proved to be a mixture of *p*-tolyl mustard-oil and *p*-tolylimido carbonyl chloride by treating with an excess of *p*-toluidine, which gave 4.5 grams sulphocarbtoluide and 1.1 grams *α*-tri-*p*-tolylguanidine. This reaction may be explained in two ways: The sulphur dichloride may first act simply as a chlorinating agent, giving the imidocarbonyl chloride and sulphur monochloride, which reacts with more isonitrile, giving mustard-oil; or the sulphur dichloride may add to the isonitrile, giving $p\text{-}CH_3.C_6H_4.N=C<^{Cl}_{S.Cl}$. That this body should be unstable—easily giving mustard-oil and imidophosgene—is likely, from the fact that no similar body has been observed in the preparation of phenylimidocarbonyl chloride by the chlorination of phenyl mustard-oil,[1] which should give $C_6H_5.N=C<^{Cl}_{S.Cl}$ as an intermediate product.

Action of Hydrogen Sulphide.—That phenyl isocyanide adds sulphuretted hydrogen was shown by Hofmann.[2] Nef[3] has obtained thioform-*o*-toluide by the action of an alcoholic solution of hydrogen sulphide on *o*-tolyl isocyanide. Paratolyl isocyanide gives the corresponding para derivative. 50 cc. of 98-per cent. alcohol were saturated with sulphuretted hydrogen at 0°; 2 grams of *p*-tolyl isocyanide were added, and the mixture was heated in a sealed tube for eight hours at 100°. On cooling, brown needles separated out, and more were obtained from the mother-liquor by evaporation, giving in all 1.1 grams crude product. This was recrystallized from ligroïn (boiling-point 70°–80°), using animal charcoal; and twice from benzene, giving nearly colorless, flat needles that melted at 175°–176°. Dried *in vacuo* over sulphuric acid and analyzed by the method of Carius:

0.1573 gram substance gave 0.2405 gram $BaSO_4$.

	Calculated for C_8H_9NS.	Found.
S	21.19	21.04

Senier[4] obtained thioform-*p*-toluide from form-*p*-toluide and phosphorus pentasulphide. He describes it as a yellow substance melting at 173.5°.

[1] Sell and Zierold: Ber. d. chem. Ges. **7**, 1228; Nef: Ann. Chem. (Liebig) **270**, 284.
[2] Ber. d. chem. Ges. **10**, 1095. [3] Ann. Chem. (Liebig) **270**, 313.
[4] Ber. d. chem. Ges. **18**, 2295.

Paratolylimido thioformic ethyl ester,

$$CH_3.C_6H_4.N=C<^{H}_{S.C_2H_5}.—$$

5 grams *p*-tolyl isocyanide and 2.5 grams ethyl mercaptan were heated in a sealed tube for two and one-half hours at 100°. The reaction was not complete at this point, for on opening the tube the odor of each of the substances could be distinguished. The product was heated on a water-bath to drive off the unchanged mercaptan and then distilled. On the second distillation 3 grams of a slightly yellow oil were obtained, which boiled at 250°–252°. On analysis:

0.2080 gram substance gave 0.1355 gram H_2O and 0.5101 gram CO_2.

0.2712 gram substance gave 18.6 cc. N at 17.5° and 744.7 mm.

0.1659 gram substance gave 0.2133 gram $BaSO_4$ (Carius).

	Calculated for $C_{10}H_{13}NS$.	Found.
C	67.04	66.88
H	7.26	7.24
N	7.82	7.81
S	17.87	17.69

The odor of this ester is disagreeable, reminding one of the imido ethers and also of sulphur derivatives. By treatment with aqueous hydrochloric acid it is converted into di-*p*-tolylformamidine hydrochloride.[1] Wallach and Wusten[2] have obtained *p*-tolylimido-thioacetic ethyl ester (boiling-point, 271°–273°) and phenylimido-thioformic methyl ester (boiling-point, 230°–240°). These with hydrochloric acid give corresponding amidines.

Paratolylimidoformic ethyl ester, $CH_3.C_6H_4.N=C<^{H}_{O.C_2H_5}.—$ 5 grams *p*-tolyl isocyanide and a solution made by dissolving 1 gram sodium in 20 cc. absolute alcohol were heated in a sealed tube for six hours at 120°. No smell of isonitrile was left. On pouring the contents of the tube into quite a quantity of water, a brown ethereal oil separated out. This was taken up with ether, and the solution, after washing to get rid of alcohol, was dried over calcium chloride. The ether was distilled off and the residue fractioned. Most of it came over between 227° and 234°. This

[1] This substance was obtained so often in this work that an analysis of it each time was deemed unnecessary. See page 380: action of amines.

[2] Ber. d. chem. Ges. **16**, 144.

fraction (4.1 grams) was redistilled, boiling at 231°–232° at 743 mm. On analysis:

0.2072 gram substance gave 0.1488 gram H_2O and 0.5572 gram CO_2.

0.2375 gram substance gave 19.1 cc. N at 23° and 736.1 mm.

	Calculated for $C_{15}H_{13}NO$.	Found.
C	73.62	73.33
H	7.97	7.98
N	8.59	8.82

This imido-ether is a pleasant-smelling oil of a slightly yellow color. On cooling to about 0° it solidifies to a crystalline solid which melts at 8°. By treatment with aqueous hydrochloric acid (dilute or concentrated), it could be converted into di-*p*-tolylformamidine hydrochloride, which gave the free base melting at 140°.

Action of Methyl Alcohol.—5 grams *p*-tolyl isocyanide and a solution made by dissolving 1 gram sodium in 10 cc. methyl alcohol were heated in a sealed tube for three hours at 130°. On cooling, quite a quantity of crystals, 2 grams, separated out. After recrystallization from alcohol, they melted at 140° and were identified with di-*p*-tolylformamidine obtained by other methods. The filtrate was poured into an excess of water. The oil which separated out was taken up with ether, and the ethereal solution, after washing several times with water, was dried over calcium chloride. The ether was then evaporated and the residue distilled, giving about a cubic centimeter of a slightly yellow oil which boiled between 215° and 220°. This was undoubtedly *p*-tolylimidoformic methyl ester (boiling-point, 216°–218°),[1] for it resembled the ethyl ester in odor and appearance, and on treatment with dilute hydrochloric acid gave di-*p*-tolylformamidine.

The above experiments make plain the reason for the failure of former attempts to obtain the alcohol addition-products of the isonitriles. The treatment has been too energetic, and the unstable imido-ethers have gone over at the temperature of the reaction to formamidines.

Reduction of Paratolyl Isocyanide.—Nascent hydrogen converts *p*-tolyl isocyanide into monomethyl-*p*-toluidine. 8 grams isonitrile were dissolved in 70 cc. amyl alcohol; the solution was heated to boiling in a flask with reversed condenser attached, and

[1] Comstock and Clapp: This Journal **13**, 527.

7.5 grams sodium gradually added. As soon as the sodium had all disappeared, the solution was cooled and washed with water. The smell of isocyanide had all disappeared. The solution was then partially dried with lime and distilled. After the amyl alcohol had distilled out, 4 grams of slightly colored oil came over between 180° and 215°, 3.5 grams between 215° and 225°, and 3 grams between 225° and 250°. These fractions were then treated with dilute hydrochloric acid. The first two gave no precipitate, but the third gave 0.4 gram of di-*p*-tolylformamidine hydrochloride, probably due to the decomposition of *p*-tolylimidoformic amyl ester, which could very easily be formed during the reaction. The acid solution was heated on the water-bath till all odor of amyl alcohol had disappeared. It was then treated with sodium nitrite, and the nitrosamine extracted with ether. After repeated crystallizations from alcohol and ether, it melted at 48°–49°. This nitrosamine was reduced with tin and hydrochloric acid. The base was then set free, distilled with steam, and the distillate extracted with ether. After drying with caustic potash, distilling off the ether, and distilling the residue, 2.5 grams of monomethyl-*p*-toluidine were obtained which boiled at 208°. On treatment with acetic anhydride, methylacet-*p*-toluide[1] was obtained, which, after several crystallizations from ligroïn, melted at 79°.

Action of Amines.—Weith[2] has shown that phenyl isocyanide unites with aniline to give diphenylformamidine. This observation has been confirmed by Nef,[3] who also obtained di-*o*-tolylformamidine[4] from *o*-tolyl isocyanide and *o*-toluidine.

4 grams *p*-tolyl isocyanide were mixed with 5 grams *p*-toluidine and heated on a metal-bath to a temperature of about 200°. Much polymerization took place, but di-*p*-tolylformamidine could be separated from the resultant tarry mass by means of boiling ligroïn (boiling-point, 70°–80°), in which it is somewhat soluble. After several recrystallizations from ligroïn, and one from alcohol, 2 grams of colorless needles was obtained, which melted at 140°.[5]

In a nitrogen determination 0.0837 gram substance gave 9 cc. N at 16° and 749.4 mm.

Calculated for $C_{15}H_{16}N_2$.	Found.
12.5	12.4

[1] Thomson: Ber. d. chem. Ges. **10**, 1582.
[2] Ber. d. chem. Ges. **9**, 454.
[3] Ann. Chem. (Liebig) **270**, 281.
[4] *Ibid.* **270**, 312.
[5] Senier: Ber. d. chem. Ges. **18**, 2296; Comstock and Clapp: This Journal **13**, 527.

A much smoother reaction is obtained by means of the amine hydrochlorides in alcoholic solution, or even in water solution in contact with an ethereal solution of the isocyanide. On mixing alcoholic solutions of the substances in the cold, no immediate reaction is noticeable; but after standing for a very few minutes, a bulky precipitate of white needles separates out, which, if the solution is not too dilute, entirely fills the liquid. This precipitate is the hydrochloride of di-*p*-tolylformamidine, and from it the free base can be easily obtained by means of alkalies. This reaction does not seem to take place quantitatively, for the yield is never equal to the theoretical, nor does the odor of isonitrile disappear from the solution even if the amine hydrochloride is present in slight excess.

On mixing aniline hydrochloride and *p*-tolyl isocyanide in alcoholic solution, a similar crystalline hydrochloride is obtained; but neither this salt nor the free base obtained from it could be obtained of constant melting-point and composition. The mixed dialkylated formamidine seems to tend to go over into a mixture of the two simple ones. This result is entirely analogous to that obtained by Nef[1] with the phenyl-*o*-tolylformamidine. Monoethylaniline hydrochloride reacts similarly, but the product of the reaction was not investigated. Diethylaniline hydrochloride does not react, neither does phenylhydrazine hydrochloride nor ammonium chloride.

The isonitriles seem to react with all substances that contain a halogen atom loosely bound. Nef[2] has proved that the aromatic isocyanides react with the free halogens. Gautier[3] has shown that the aliphatic derivatives react with the haloid acids, and Nef[4] has obtained the same result with phenyl isocyanide. Nef[5] has also shown that the aromatic isocyanides add organic-acid chlorides, giving imide chlorides.

I have studied the reactions of *p*-tolyl isocyanide with a large number of chlorides. With hydrochloric acid, either dry or aqueous, it reacts with great violence. The reaction seems to be the same as in the case of the other isonitriles and the reaction-product was not carefully studied. With the chlorides of the negative elements it reacts in all cases tried, but in most cases[6] it does not

[1] Ann. Chem. (Liebig) **270**, 312.
[2] *Ibid.* **270**, 282, 313, 321.
[3] Ann. chim. phys. [4] **17**, 222 and 239.
[4] Ann. Chem. (Liebig) **270**, 303.
[5] *Ibid.* **270**, 286 and 315 *et seq.*
[6] See reaction with chlorides of sulphur, page 375.

seem to be possible to isolate the addition-products, since they immediately decompose, giving the original chloride and isocyanide which in this nascent state entirely polymerizes. With the organic-acid chlorides, however, much more tangible results were obtained.

Mesoxalparatoluide hydrate, $CH_3.C_6H_4.N=C<\begin{matrix}OH\\C<OH\\OH\end{matrix}$ $CH_3.C_6H_4.N=C<\begin{matrix}OH\\C<OH\\OH\end{matrix}$ —.

Phosgene reacts very energetically with *p*-tolyl isocyanide. A smooth reaction was obtained as follows: 9.5 grams *p*-tolyl isocyanide were mixed with a little more than an equal volume of absolute ether and cooled in a mixture of salt and snow. 10 cc. of phosgene, previously cooled in a freezing-mixture, were added, and the mixture was allowed to warm slowly to the temperature of the room, moisture being excluded by a chloride-of-calcium tube. After standing for thirty-six hours, it was heated for a short time on the water-bath to drive off the excess of phosgene. The reaction-product was a thick oil, colored dark by polymerized isonitrile, but was without a trace of isonitrile odor. It was not attempted to purify this imide chloride directly, but instead it was poured into an excess of cold water. It became solid slowly, without any marked evolution of heat. After pulverizing and treating thoroughly with cold water, the solid was filtered off and dried. From this crude product, mesoxal-*p*-toluide hydrate was obtained in a pure state by boiling with water, or more rapidly, by digestion with dilute alkalies.

It is almost insoluble in cold water, and a litre of boiling water dissolves only about 0.25 gram, which crystallizes out on cooling in the form of fine colorless needles. These, pulverized and dried *in vacuo* over sulphuric acid, gave the following figures on analysis:

0.1841 gram substance gave 0.0969 gram H_2O and 0.4346 gram CO_2.

0.1897 gram substance gave 0.4508 gram CO_2 (H_2O lost).

0.1830 gram substance gave 14.2 cc. N at 9° and 757 mm.

	Calculated for $C_{17}H_{18}N_2O_4$.	Found.	
C	64.97	64.39	64.80
H	5.73	5.85	...
N	8.92	9.31	...

If heated rapidly the hydrate becomes yellow at a little above 100°, and melts to a sticky resinous mass at 120°–130°. If heated

more slowly, the water goes off gradually and the residue melts at 187°. Mesoxal-*p*-toluide hydrate has acid properties. It does not color litmus, but it dissolves in sodic hydrate and is precipitated unchanged by hydrochloric acid. It dissolves readily in most organic solvents, but on heating these solutions they become yellow, showing the conversion of the toluide hydrate into the toluide. Both the pure hydrate and the crude product mentioned above are readily soluble in alcohol, being converted thereby more or less completely into

Mesoxalparatoluide alcoholate, $\begin{matrix} CH_3.C_6H_4.N=C<^{OH}_{C<^{OH}_{OC_2H_5}} \\ CH_3.C_6H_4.N=C \end{matrix}$.

—This was obtained chiefly from the crude product by dissolving in alcohol and precipitating with water and then recrystallizing from dilute alcohol and dilute acetone. In order to be sure that the hydrate was all converted into the alcoholate, it was finally dissolved in absolute alcohol and boiled for an hour in a flask, to which a reversed condenser was attached. Then the alcohol was partly distilled off and, on cooling, the alcoholate crystallized out in colorless microscopic needles. Pulverized and dried over sulphuric acid *in vacuo*, they gave the following analytical figures:

0.1429 gram substance gave 0.0897 gram H_2O and 0.3491 gram CO_2.

0.2439 gram substance gave 16.6 cc. N at 9° and 752 mm.

	Calculated for $C_{19}H_{22}N_2O_4$.	Found.
C	66.66	66.61
H	6.43	6.97
N	8.19	8.12

In its physical properties the alcoholate resembles the hydrate very closely. By treatment with water a small quantity dissolves, being probably converted into the hydrate.

On heating, the alcoholate loses alcohol quantitatively, as the following experiment proves:

0.3965 gram alcoholate heated 3 hours at 95° lost 0.0432 gram.

3 hours at	105°–115°	"	0.0023 "
8 hours at	95°–130°	"	0.0045 "
3 hours at	110°–120°	"	0.0021 "
3 hours at	110°–120°	"	0.0010 "
3 hours at	110°–120°	"	0.0000 "
23 hours at	90°–130°	"	0.0531 "

Calculated for loss of C_2H_4O.	Found.
13.45	13.49

The yellow powder left behind was

Mesoxalparatoluide, $\begin{matrix} CH_3.C_6H_4.N=C<OH \\ CH_3.C_6H_4.N=C< \end{matrix}C=O$.—It was analyzed without further treatment:

0.1402 gram substance gave 0.0714 gram H_2O and 0.3542 gram CO_2.

	Calculated for $C_{17}H_{16}N_2O$.	Found.
C	68.92	68.87
H	5.41	5.66

Its melting-point was found to be 187°. It is soluble in the ordinary organic solvents, giving yellow solutions in such as contain no water or alcohol; but if these are present the solution is colorless and the substance is converted into the hydrate or alcoholate. It reacts with phenylhydrazine, but the reaction-product was not investigated.

Benzoylformoparatoluide, $CH_3.C_6H_4N.=C<\begin{matrix} OH \\ CO.C_6H_5 \end{matrix}$.—Benzoyl chloride and *p*-tolyl isocyanide react slowly on each other. 8 grams isonitrile and 9.6 grams benzoyl chloride were heated on a water-bath in a flask closed by a chloride-of-calcium tube, for ten hours. The smell of isonitrile had all disappeared, but polymerization had taken place to a considerable extent. In order to remove the polymerization-product, the tarry mixture was boiled out with several volumes of ligroïn (boiling-point, 70°–80°) and filtered hot. After distilling off the ligroïn, water was added to decompose the chlorides, and the mixture was heated on the water-bath till all smell of benzoyl chloride had disappeared. The resultant solid was dissolved in ether and the solution washed with sodium carbonate to remove benzoic acid. After drying with calcium chloride the ether was partially distilled off, and the benzoylformic-*p*-toluide was allowed to crystallize out. After recrystallization from alcohol, ether, and finally from ligroïn, flat yellow needles were obtained which melted at 111°–113°. On analysis:

0.1350 gram substance gave 0.0718 gram H_2O and 0.3741 gram CO_2.

0.3738 gram substance gave 20.25 cc. N at 25° and 749 mm.

	Calculated for $C_{10}H_{13}NO_2$.	Found.
C	75.31	75.54
H	5.44	5.91
N	5.86	5.99

This substance is very slightly soluble in hot water, but is quite soluble in hot sodic-hydrate solution (1 : 30), from which it crystallizes unchanged on cooling and may also be precipitated by acids.

Pyruvic paratoluide, $CH_3.C_6H_4.N = C < \begin{matrix} OH \\ COCH_3 \end{matrix}$. — Acetyl chloride reacts with *p*-tolyl isocyanide much more readily than benzoyl chloride. If a mixture of these two substances be incautiously heated, the reaction is so violent that the whole mass chars. The addition was accomplished as follows: 9.5 grams of *p*-tolyl isocyanide and 7 grams acetyl chloride were mixed in a flask at the ordinary temperature. A reversed condenser closed by a chloride-of-calcium tube was attached and the flask was placed in a cold-water bath, which was then slowly heated to the boiling-point. After the water had boiled four minutes the flask was removed. As soon as the contents of the flask had cooled they were poured into 200 cc. of ice-water. After the mass had become solid it was pulverized and again treated with water, then filtered off and dried. 10 grams of crude product were obtained. This was recrystallized from 2.5 liters boiling water and finally from alcohol, giving 5 grams colorless scales which melted at 108°. On analysis:

0.1793 gram substance gave 0.1040 gram H_2O and 0.4460 gram CO_2.

0.2314 gram substance gave 16.7 cc. N at 13.5° and 754 mm.

	Calculated for $C_{10}H_{11}NO_2$.	Found.
C	67.79	67.83
H	6.21	6.44
N	7.91	8.47

It is easily soluble in boiling alcohol or ether, from which it crystallizes on cooling. It dissolves readily in cold 10-per cent. sodic-hydrate solution; on adding an acid, however, the original compound is not precipitated, but a substance that seems to be a mixture of a hydrate and a polymer; for if it is heated it becomes soft at 60°–70°, and if warmed with water becomes sticky and a

part (the hydrate) goes into solution while the polymer remains behind. The same change seems to take place to some extent when pyruvic *p*-toluide is dissolved in water, for, on allowing the aqueous mother-liquor from which the toluide was originally crystallized, to stand for some days in the cold, quite a quantity of the polymer separated out. If the sodic-hydrate solution of pyruvic *p*-toluide is made very dilute, the addition of acid produces no precipitate, but, on extracting with ether, a clear ethereal solution is obtained, from which, on standing in the cold, the polymer very slowly separates out in the form of colorless microscopic prisms. This polymer melts at 193°–194°. It is very slightly soluble in water, alcohol, and ether, and somewhat more readily in chloroform. On analysis:

0.1145 gram substance gave 0.0664 gram H_2O and 0.2783 gram CO_2.

0.1311 gram substance gave 0.0818 gram H_2O and 0.3275 gram CO_2.

0.2087 gram substance gave 14.6 cc. N at 22° and 745.6 mm.

	Calculated for $(C_{10}H_{11}NO_2)_m$.	Found.	
C	67.79	66.28	68.12
H	6.21	6.44	6.93
N	7.91	7.85	...

Action of Phenylhydrazine on Pyruvic Paratoluide.—On mixing in the cold an ethereal or alcoholic solution of pyruvic *p*-toluide with the calculated (1 mol.) amount of phenylhydrazine, a substance quickly begins to separate out in the form of microscopic needles. This precipitate is very bulky, soon filling the entire solution when in the proportion of 1 gram pyruvic *p*-toluide to 50 cc. solvent. The reaction never seems to be complete and the calculated quantity is never obtained. This reaction-product is pyruvic-*p*-toluide phenylhydrazone hydrate, but it loses water so readily that it could not be analyzed. It was prepared for analysis by drying on a clay plate, being pressed between filter-papers, and standing *in vacuo* over sulphuric acid for one hour.

Analyses of three different preparations gave varying figures, all between the hydrazone and the hydrazone hydrate. On heating the freshly precipitated hydrazone hydrate in a capillary tube it partially melts at about 100°, then becomes solid again and finally melts at about 200°. On heating 0.409 gram in an

open dish for five hours at 115° in an air-bath it lost 0.0202 gram and did not change in weight by the further heating. If it had been pure hydrazone hydrate it should have lost 0.0259 gram.

Pyruvic-paratoluide phenylhydrazone, $CH_3.C_6H_7.N=C\text{-}OH$ / $C_6H_5.NH\text{-}N=C\text{-}CH_3$.

—The product obtained by heating the hydrate was crystallized once from alcohol. It then melted at 204°. On analysis:

0.1671 gram substance gave 23.5 cc. N at 16° and 746.3 mm.

0.1335 gram substance gave 0.0777 gram H_2O and 0.3497 gram CO_2.

	Calculated for $C_{17}H_{17}N_3O$.	Found.
C	71.91	71.44
H	6.37	6.47
N	15.72	16.15

This hydrazone can be obtained more simply by heating the hydrazone hydrate in ethereal or alcoholic solution.

The proof that the above bodies are derivatives respectively of mesoxalic, benzoylformic, and pyruvic acids is unnecessary, as it has already been given by Nef[1] in the case of corresponding anilides and orthotoluides.

Action of Formic Acid.—Paratolyl isocyanide reacts with formic acid in the same way as do the other isocyanides that have been carefully studied.[2] 4 grams *p*-tolyl isocyanide were added to the calculated amount (two molecules) of crystallized formic acid at 0°. A lively evolution of gas took place at once. The residue was distilled, giving 3 grams of an oily substance which on crystallization from ether and ligroïn gave colorless crystals melting at 54° and identical with formo-*p*-toluide as described by Tobias.[3]

Molecular Rearrangement.—The molecular rearrangement of the isocyanides by heat was first noticed by Weith[4] in the case of phenyl isocyanide. Hofmann[5] obtained the rearrangement of the isocyanides derived from pentamethylamidobenzene and tetramethylamidobenzene. Nef[6] has obtained *o*-tolyl cyanide from *o*-tolyl isocyanide. 5 grams *p*-tolyl isocyanide were heated in a sealed tube for three hours at 210°–225°. On opening the tube

[1] Ann. Chem. (Liebig) **270**, 293, 302, 320.
[2] Gautier: Ann. chim. phys. [4] **17**, 223, 241; Nef: Ann. Chem. (Liebig) **270**, 278, 310.
[3] Ber. d. chem. Ges. **15**, 2446. [4] *Ibid.* **6**, 213.
[5] *Ibid.* **17**, 1914; **18**, 1824. [6] Ann. Chem. (Liebig) **270**, 311.

the isonitrile smell had entirely disappeared, but much polymerization had taken place. The product was taken up with dry ether to get rid of the polymerized isocyanide. After distilling off the ether the residue was distilled, yielding 3 grams of *p*-tolyl cyanide boiling at 213°–214° and melting at 27°. Paterno and Spica[1] give as the boiling-point 217°–218°, and as the melting-point, 28.5°. Its identity was further proved by saponification with sulphuric acid, giving *p*-tolylic acid[2] melting at 180°.

Paratolyl Isocyanide and Silver Cyanide.—If *p*-tolyl isocyanide and silver cyanide are mixed in the cold, a noticeable evolution of heat ensues, and the mass on being thoroughly mixed becomes solid. 2 grams *p*-tolyl isocyanide and an equal quantity of silver cyanide were mixed in a mortar and rubbed till a dry powder ensued. This was boiled out with 2 liters of water, and on cooling 0.6 gram colorless needles crystallized out. These were filtered off, dried on a clay plate, pressed between filter-papers and analyzed:

0.1537 gram substance gave 0.0511 gram H_2O and 0.2751 gram CO_2.

0.1544 gram substance gave 15.5 cc. N at 21° and 750.8 mm.

0.2165 gram substance gave 0.1055 gram AgCl (Carius).

0.1092 gram substance gave 0.0380 gram H_2O and 0.1916 gram CO_2.

0.1288 gram substance gave 0.0629 gram AgCl (Carius).

Calculated for $\left\{\begin{matrix}AgNC\\C_7H_7NC,\end{matrix}\right.$		for $\left\{\begin{matrix}2AgNC\\3C_7H_7NC.\end{matrix}\right.$	Found.	
C	43.03	50 48	48.81	48.96
H	2.79	3.39	3.69	3.87
Ag	43.03	34.84	36.67	36.76
N	11.16	11.29	11.34	...

It melts at 118° with decomposition. On boiling out the residue with as much more water more material is obtained, but this does not seem to be as pure and is not so well crystallized. If the clear solution first obtained be boiled for a few moments it becomes turbid from the silver cyanide which separates out. If the crystalline product be washed with alcohol or ether it is decomposed and the residue is much poorer in carbon and hydrogen, as was proved by analysis. The substance is decomposed by heating with potassium-cyanide solution, drops of

[1] Ber. d. chem. Ges. **8**, 441. [2] Fischli: Ber. d. chem. Ges. **12**, 615.

isonitrile separating out. It is also decomposed by hydrochloric acid, giving silver cyanide. The product and its solutions always smell of isonitrile.

The above experiments agree very well with the supposition that a simple double salt is first formed and that this is then decomposed by the water from which it was crystallized. This is in accordance with the results of Meyer,[1] who obtained a double salt $AgNC.C_6H_5NC$, which was decomposed by alcohol, ether, potassium cyanide, dilute acids, and even by standing in the air. Hofmann[2] states that phenyl isocyanide easily unites with other cyanides, the compound with silver cyanide crystallizing especially well. In the case of *p*-tolyl isocyanide I have been unable to obtain evidence of reaction with any of the metallic cyanides at my disposal, except with silver cyanide.

As was shown by the experiments of Nef[3] the isocyanides easily add two atoms of chlorine, forming alkylated imidophosgenes. These products can be more easily obtained, however, by the action of chlorine on the mustard-oils. From the constitutional resemblance of these compounds to phosgene I was led to investigate the action of sodium alcoholates upon one of them, and found that the analogy of the reactions was very striking. When phenylimidophosgene is treated with sodium alcoholates under the proper precautions, it gives phenylimidochlorformic esters, only one atom of chlorine reacting:

$$C_6H_5.N:C\langle{Cl \atop Cl} + NaOR = C_6H_5.N:C\langle{Cl \atop OR} + NaCl.$$

Under more energetic treatment, however, both chlorine atoms react, giving phenylimidocarbonic esters.

$$C_6H_5.N:C\langle{Cl \atop Cl} + 2NaOR = C_6H_5.N:C\langle{OR \atop OR} + 2NaCl.$$

Phenylimidocarbonyl chloride was prepared from phenyl mustard-oil, according to Nef's modification[4] of the method of Sell and Zierold.[5] A 90-per cent. yield was obtained.

Phenylimidochlorformic ethyl ester, $C_6H_5N=C\langle{Cl \atop OC_2H_5}$.—This substance was first prepared by digesting an excess of dry sodium ethylate with an absolute-ethereal solution of phenylimidocarbonyl chloride. This method goes very well, but it is

[1] J. prakt. Chem. **68**, 285. [2] Ann. Chem. (Liebig) **144**, 118.
[3] *Ibid.* **270**, 289, 313, 321. [4] *Ibid.* **270**, 284. [5] Ber. d. chem. Ges. **7**, 1228.

much simpler to use an alcoholic solution of sodium ethylate, as was suggested by Stieglitz and Lengfeld.[1] 17.4 grams phenylimidophosgene were dissolved in a cold mixture of equal parts (15 cc. each) absolute alcohol and dry ether. To this was slowly added a solution obtained by dissolving 2.3 grams sodium in an appropriate quantity of absolute alcohol. An evolution of heat and separation of sodium chloride were at once noticeable. The mixture was kept in a dish of ice-water during the reaction and for about five minutes thereafter. It was then poured into an excess of water, extracted with ether, and the ethereal solution washed six times with water. By extracting the first washings again with ether a considerable increase in the yield can be obtained. The solution was dried with calcium chloride and the ether distilled off (either *in vacuo* or at ordinary pressure). An almost colorless oil was obtained which boiled at 105° at 12 mm. pressure, yielding 16 grams of a colorless, sweet-smelling oil which gave the following figures on analysis:

0.1041 gram substance gave 0.0556 gram H_2O and 0.2247 gram CO_2.

0.2467 gram substance gave 17 cc. N. at 22° and 749.3 mm.

0.3200 gram substance gave 0.2511 gram AgCl (Carius).

	Calculated for $C_9H_{10}NOCl$.	Found.
C	58.84	58.87
H	5.45	5.93
N	7.63	7.73
Cl	19.34	19.42

The combustion must be carried out with great care, as ethyl chloride is easily split off. The same holds true of the Carius determination. It was found necessary to heat for eight hours at 180°, finally raising the temperature to 225° for an hour.

Phenylimidochlorformic ethyl ester has a specific gravity of 1.144 at 12° (Westphal). It boils at ordinary pressure with slight decomposition, the distillate smelling of phenyl isocyanate. It is quite stable towards water and alkalies, but is easily decomposed by acids. With concentrated hydrochloric acid a violent reaction soon ensues, the ester being split into phenyl isocyanate, which, under the influence of the acid, gives carbanilide, and ethyl chloride, which is given off with ebullition. The same decomposition

[1] This Journal **16**, 73.

takes place slowly if the ester is allowed to stand in damp air, but it can be kept indefinitely in a desiccator over potassium hydrate.

The action of aniline on this substance was carefully studied. The reaction is

$$C_6H_5N:C\begin{matrix}Cl\\O-C_2H_5\end{matrix} + 2C_6H_5NH_2 =$$
$$(C_6H_5NH)_2CO + C_6H_5NHC_2H_5.HCl,$$

as the following experiment proves: 0.7 gram of aniline and an equal amount of the chlorformic ester were carefully mixed in the cold. The mixture was cooled by means of ice till it became solid. It was then gently warmed and treated with cold water acidified with hydrochloric acid. A part went into solution and there was left behind 0.6 gram carbanilide, melting at 235°.[1] The filtered acid solution was made alkaline, giving an oil having the odor of an alkylated aniline. This was taken up with ether, dissolved in an excess of dilute hydrochloric acid, and treated with sodium nitrite. A brown oil separated out, which was volatile with steam, had the characteristic odor of the nitrosamines, and gave Liebermann's reaction with phenol and concentrated sulphuric acid.

Werner[2] has obtained the above-mentioned ester in an impure state by the action of phosphorus pentachloride on ethylsynbenz. hydroxamic acid.

Phenylimidocarbonic diethyl ester, $C_6H_5.N=C\begin{matrix}O.C_2H_5\\O.C_2H_5\end{matrix}$—

After one of the chlorine atoms in phenylimidophosgene has been replaced by the ethoxy group, the second is replaced with much more difficulty. On treating phenylimidocarbonyl chloride in the cold with an alcoholic solution of two molecules of sodium ethylate, the replacement is not complete, but a mixture of chlorformic and carbonic esters results. The best method of procedure was found to be slowly to pour a solution of phenylimidophosgene in dry alcohol and ether into an alcoholic solution of two molecules sodium ethylate, allowing the temperature to rise to about 50°. After standing for half an hour at this temperature the mixture is poured into water and extracted with ether. The ether, after drying with calcium chloride, was distilled off, leaving a colorless oil which, on the second distillation at reduced pressure, boiled at 122° at 12 mm. On analysis:

0.2018 gram substance gave 13.5 cc. N at 20° and 748.5 mm.

[1] Weith: Ber. d. chem. Ges. **9**, 820. [2] Ber. d. chem. Ges. **25**, 38; **26**, 1565.

0.1358 gram substance gave 0.3416 gram CO_2 and 0.1009 gram H_2O.

0.1547 gram substance gave 0.3889 gram CO_2 and 0.1089 gram H_2O.

	Calculated for $C_{11}H_{13}NO_2$.	Found.	
C	68.39	68.61	68.54
H	7.77	8.25	7.85
N	7.26	7.57	...

The combustion must be conducted with great care, as the compound seems to decompose into gaseous products which are liable to go over unburned. On heating 5 grams of this substance in a sealed tube for five hours at 300° it was completely decomposed and there could be isolated as decomposition-products, aniline, carbanilide and a gas consisting largely of carbon dioxide and unsaturated hydrocarbons.

Phenylimidocarbonic diethyl ester is a colorless and nearly odorless oil. It boils at ordinary pressure at about 245° with some decomposition, as the distillate always smells of phenyl isocyanate. It is stable towards alkalies and water, but is split by dilute hydrochloric acid in the cold—more quickly on warming—into aniline and carbonic diethyl ester. This resembles the decomposition of imidocarbonic diethyl ester, $NH=C<^{OR}_{OR}$, obtained by Sandmeyer,[1] which is split by acids into ammonia and carbonic ester. Sandmeyer also obtained by the action of aniline hydrochloride on the imidocarbonic ester an oil which he was not able to purify, but which he considered to be the phenylimidocarbonic diethyl ester described above.

Phenylimidochlorformic methyl ester, $C_6H_5.N=C<^{Cl}_{OCH_3}$.—This was made from phenylimidophosgene and a solution of sodium methylate in methyl alcohol in exactly the same manner as the ethyl ester was made from sodium ethylate. It is a colorless, pleasant-smelling oil, exactly analogous to the ethyl ester. It boils at 104° at 15 mm. pressure, and with very slight decomposition at 215° at ordinary pressure. On analysis,

0.1734 gram substance gave 0.3597 gram CO_2 and 0.0782 gram H_2O.

0.2498 gram substance gave 17.8 cc. N at 20.5° and 754.5 mm.

0.1765 gram substance gave 0.1510 gram AgCl (Carius).

[1] Ber. d. chem. Ges. **19**, 864.

Calculated for C_8H_8NOCl.	Found.	
C	56.64	56.56
H	4.72	5.02
N	8.26	8.11
Cl	20.94	21.17

Phenylimidocarbonic dimethyl ester, $C_6H_5.N=C<^{OCH_3}_{OCH_3}$.—This compound was made by pouring a solution of phenylimidophosgene in dry ether and alcohol into a methyl-alcohol solution of two molecules sodium methylate, at a temperature of about 50°. The mixture was poured into water, the oil taken up with ether, and, after drying and distilling off the ether, distilled at reduced pressure. It boils at 123.5° at 16 mm. pressure. On analysis:

0.1610 gram substance gave 0.3847 gram CO_2 and 0.0982 gram H_2O.

0.2338 gram substance gave 17.2 cc. N at 18° and 748.8 mm.

	Calculated for $C_9H_{11}NO_2$.	Found.
C	65.44	65.15
H	6.67	6.78
N	8.48	8.40

It is a colorless oil, of very slight odor, entirely analogous to the diethyl ester. Treated with aniline in the cold it gives carbanilide. Treated with aniline hydrochloride in methyl-alcohol solution it gives the same product.

Phenylimidochlorformic phenyl ester, $C_6H_5.N=C<^{Cl}_{OC_6H_5}$.—8.7 grams phenylimidophosgene were dissolved in 20 cc. absolute ether and an equal quantity of absolute alcohol was added. The mixture was cooled with ice-water, and to it was slowly added a solution made by dissolving 1.15 grams sodium in absolute alcohol and adding to it 4.7 grams phenol. An immediate precipitation of sodium chloride was noticeable. The mixture was kept cold with ice for a few minutes and then allowed to stand in a dish of cold water for two hours. It was then poured into an excess of cold water and the oil taken up with ether. The ethereal solution was washed with sodic hydrate to remove any excess of phenol and then repeatedly washed with water. After drying with calcium chloride, the ether was distilled off and the residue distilled at reduced pressure. The oil commenced to boil

at about 100° (12 mm.). The thermometer quickly rose to 164°, and the main fraction (7 grams) distilled between 164° and 168°. This was redistilled, boiling at 168° at 12 mm. pressure. On analysis:

0.2096 gram substance gave 0.0880 gram H_2O and 0.5194 gram CO_2.

0.3932 gram substance gave 21.4 cc. N at 23.5° and 748.3 mm.

0.2040 gram substance gave 0.1257 AgCl (Carius).

	Calculated for $C_{13}H_{19}NClO$.	Found.
C	67.39	67.57
H	4.32	4.66
N	6.05	6.06
Cl	15.33	15.25

This ester is a colorless oil which has an odor resembling the ethyl ester, but much fainter. On cooling it solidifies to a white crystalline solid which melts at 43°. It is quite stable toward alkalies, but with hydrochloric acid gives carbanilic phenyl ester,[1] melting at 124°. On treating with two molecules aniline and heating till a decided reaction took place, the hydrochloride of α-triphenylguanidine[2] was the only product that could be isolated from the resultant mixture. On treating with one molecule aniline and keeping the mixture cool, various mixtures of carbanilide and α-triphenylguanidine hydrochloride were obtained.

REVIEW.

A Detailed Course of Qualitative Chemical Analysis, with Explanatory Notes. By Arthur A. Noyes, Ph. D., Instructor in Chemistry in the Massachusetts Institute of Technology. 80 pp. Boston: Published by the Author.

It is a statement with which, I think, most teachers of chemistry will agree, that the results of teaching qualitative analysis to large

[1] Hofmann: Ber. d. chem. Ges. **4**, 249.

[2] Merz and Weith: Zeit. f. Chem. **1868**, 513; Hofmann: Ber. d. chem. Ges. **2**, 453.

classes are generally unsatisfactory. Few students acquire, in the time usually devoted to this study in schools and colleges, a sufficiently good knowledge of the subject to enable them to analyze a mineral or an industrial product of some complexity without the book before them which gives the scheme of analysis to which they have been accustomed, and to which they are slavishly attached. Either this condition of affairs is inherent in the subject itself, or else the usual method of teaching fails to give the student a comprehensive view of qualitative analysis which will enable him to think and work independently of books, and to adapt his methods and procedures to each particular case which may arise.

The large number of manuals on qualitative analysis which have been published express, apparently, the dissatisfaction which each teacher has felt with those already existing, and his desire to teach the subject in his own way.

Dr. Noyes' book is the outgrowth of his teaching of qualitative analysis in the Massachusetts Institute of Technology, and embodies the systematic class-room instruction in the subject which accompanies the laboratory course. The idea of the book may be thus briefly described: Under each group of metals there is given the "procedure," expressed both in text and in tabular form, giving the necessary directions for adding the different group reagents and the purpose of this addition. Then follows—and this is the most valuable feature of the work—a series of "notes" which state concisely and clearly the necessary conditions for the successful separation and identification of each metal, the complications which may arise from a faulty procedure (such as adding too much or too little of a reagent, failure to get rid of an excess of sulphuretted hydrogen or nitric acid and the like), the characteristic appearances caused by the presence of different metals—in short, all that is necessary to know and observe in conducting intelligently an ordinary qualitative analysis.

The same idea is carried out in the detection of the acids, and in this especially difficult part of qualitative analysis the author has been very successful in giving clear and precise directions which make their identification easy.

In the short limit of eighty pages Dr. Noyes has condensed the greater part of the material found in large treatises, such as Fresenius' Qualitative Analysis, and by his admirable arrangement of this material has made a book which can be put into the hands of beginners, and, as experience has shown, with the happiest results.

THOMAS M. DROWN.